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Electronic Structure of Borabenzene and Its Adducts with Carbon Monoxide and Nitrogen

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Abstract: Electronic structures of borabenzene and its adducts with carbon monoxide and nitrogen have been studied with HF/6-31G* and MP2/6-31G* molecular orbital calculations. All three molecules are predicted to be stable and possess a planar geometry. At the highest level of theory used (MP2/6-31G*) the calculated heats of formation (relative to the isolated molecules) are −39.4 and −19.2 kcal/mol for the carbon monoxide and the nitrogen adducts, respectively. The bonding between borabenzene and CO or N_2 involves a σ donation to the borabenzene molecule and a π back-donation to the CO or N_2 molecule. The sources of overestimation of the latter and underestimation of the former interactions within the Bader population analysis are discussed.

Although several complexes of borabenzene (borinine) (**1**) have been characterized[1] and some of its adducts have been synthesized,[2] the very existence of a free molecule has not been proven until very recently.[3] Flash thermolysis of a borahexadiene precursor yielded the borabenzene–nitrogen adduct (**3**) when nitrogen was used as the carrier gas. Similarly, formation of the carbon monoxide adduct (**2**) was also observed.

Borabenzene is a remarkable molecule. According to both semiempirical MNDO[4] and ab initio STO-3G and 4-31G[5] calculations **1** is planar and the π-electrons of the boron–carbon backbone are highly delocalized. Therefore **1** can be regarded as an aromatic system. However, the presence of an electron hole at the boron atom leads to a substantial distortion of the predicted geometry from that a regular hexagon. The resulting strain lowers the stabilization energy by ca. 30 kcal/mol as compared to benzene.[5] Another consequence of the boron substitution is the presence of a low-lying σ^* orbital that is responsible for a pronounced Lewis acidity and a high reactivity of borabenzene.

Since theoretical studies on **1** are scarce[4-6] and, to our knowledge, no calculations on either **2** or **3** have been reported, we decided to optimize the geometries and investigate the electronic structure of **1**, **2**, and **3** at the HF/6-31G* level.[7] The single-point energies at the MP2/6-31G* also have been computed together with the HF/6-31G* vibrational frequencies.

Details of Calculations

The SCF and MP2 calculations have been performed with a vectorized version of the GAUSSIAN-82 package.[8] The geometry optimization required ca. 20 h of combined CPU and IO times (CRAY X-MP48) per molecule. The CPU/IO time for the vibrational frequencies was ca. 5 h. The electron density has been analyzed with programs EXTREME and PROAIM developed by Bader et al.[9] The effective atomic charges have been calculated with the recently developed GAPT partitioning.[10] In this approach the atomic charge of atom A is given as an isotropically averaged atomic polar tensor[11]

$$Q^{(A)}_{\mathrm{GAPT}} = (1/3)\left[\frac{\partial \mu_x}{\partial x_A} + \frac{\partial \mu_y}{\partial y_A} + \frac{\partial \mu_z}{\partial z_A}\right] \tag{1}$$

where μ_r and r_A ($r = x, y, z$) denote the components of the dipole moment and the position vector of the nucleus A, respectively. The GAPT charges are byproducts of the computation of the IR intensities and therefore are easily available.

Results and Discussion

Both borabenzene (**1**) and its adducts (**2** and **3**) are predicted to be minima on the potential energy hypersurface. All the molecules are planar. The optimized geometry of **1** is similar to that obtained in previous 4-31G calculations,[5] but the distortion of molecule from the shape of a regular hexagon is slightly larger. The geometries of adducts **2** and **3** show several interesting features (Figure 1). First of all, the deviations of bond angles from the value of 120° are much smaller than in **1**. This is accompanied by a substantial lengthening of the $B–C_1$ bonds. Both effects are more pronounced in the CO adduct than in the N_2 one. There is a remarkable insensitivity of the geometry of the CO and N_2 parts to formation of the adducts. The respective bond lengths are within less than 0.001 Å of those in free molecules. The boron–ligand bond lengths are comparable to but shorter than the B–C bond length (HF/6-31G*:1.627 Å) in the $BH_3{\cdot}CO$ complex. This reflects the greater stability of the borabenzene adducts.

At the HF level, the stability (ΔH_{HF} in Table I) of **2** is much higher than that of **3**. When the zero-point vibrational energies (as calculated from the HF/6-31G* vibrational frequencies) are taken into account, the energy (ΔH_{HF} in parentheses, Table I) of the N_2 adduct is only ca. −3 kcal/mol lower than the sum of the energies of free molecules. Upon inclusion of the electron correlation at the MP2 level, the stability of both **2** and **3** increases by about 15 kcal/mol (ΔH_{MP2}, Table I). The MP2/6-31G* dissociation energy of the $B–C_4$ bond in **2** amounts to ca. 40% of the dissociation energy of a typical single C–C bond. The HF and MP2 stabilities of **2** and **3** can be compared to the values of −9.1 kcal/mol (HF/6-31G*) and −24.6 kcal/mol (MP2/6-31G*) for the $BH_3{\cdot}CO$ complex.

The possible orbital interactions that lead to the borabenzene–ligand bonding are conveniently classified according to their symmetries. They are as follows: the σ donation from the nonbonding σ orbitals of CO or N_2 to the low-lying antibonding σ^* of borabenzene (a_1), the π back-donation from the π orbitals of borabenzene to the vacant π^* orbitals of CO or N_2 (b_1), and the back-donation of the antisymmetrical σ orbitals of borabenzene to the vacant "in-plane" π^* orbital of CO or N_2 (b_2). The an-

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Table I. Total Energies, Heats of Formation, and Dipole Moments of Borabenzene and Its Adducts with CO and N_2[a]

	borabenzene	CO	N_2	borabenzene·CO	borabenzene·N_2
E_{HF}	−216.863 783 14	−112.737 876 95	−108.943 949 47	−329.643 527 02	−325.816 786 01
E_{MP2}	−217.596 255 18	−113.025 147 87	−109.254 562 95	−330.689 758 62	−326.881 378 56
ΔH_{HF}				−26.3 (−22.8)	−5.7 (−2.9)
ΔH_{MP2}				−42.9 (−39.4)	−19.2 (−16.4)
μ_{HF}	0.7644	0.2638	0.0000	1.3433	2.8961

[a] Entries in au, kcal/mol, and D. Values of ΔH corrected for the zero-point energies are given in parentheses. Both the uncorrected and corrected values of ΔH correspond to 0 K.

Table II. Selected HF/6-31G* Force Constants in Borabenzene Adducts and Free Molecules[a]

	free molecules	borabenzene adduct
k_{CO}	1.54	1.49
k_{NN}	2.02	1.96
k_{BC}		0.199
k_{BN}		0.099

[a] All entries in atomic units.

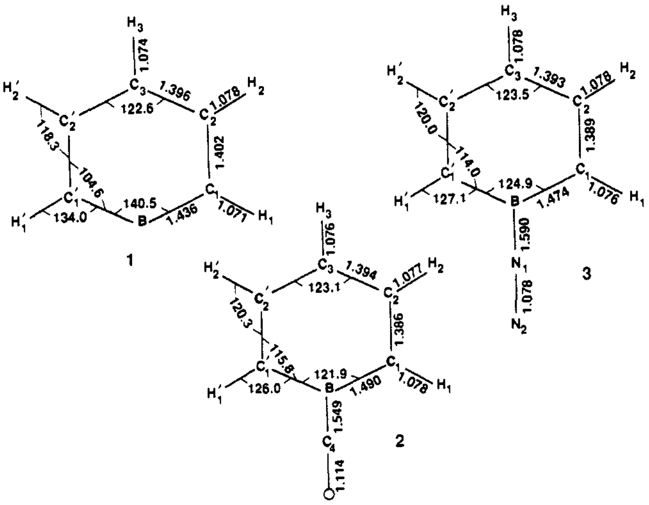

Figure 1. Optimized geometries of borabenzene (**1**) and its adducts with CO (**2**) and N_2 (**3**). Entries are in angstroms and degrees.

tisymmetrical π orbital of borabenzene (a_2) has neither CO nor N_2 counterparts.

The features of the bonds within the CO and N_2 ligands are largely preserved in adducts **2** and **3**. This is reflected in the aforementioned bond lengths (Figure 1) and force constants for the bond stretching (Table II). The topological characteristics of the bonds,[12] such as the position of the critical point ($r_{C4-Crit}$ and $r_{N1-Crit}$), the electron density at the critical point (ρ_{Crit}), and the Laplacian at the critical point ($\nabla^2\rho_{Crit}$) also change only a little (Table III). Any substantial π back-donation would result in lengthening of the CO and N_2 bonds and decrease in the respective force constants. The bonding situation in the $Ni(CO)_4$ molecule can serve as a typical example.[13] Therefore we conclude that the borabenzene–ligand bonding arises primarily from the σ donation to the vacant σ^* orbital that is mostly localized at the boron atom[4] (see also discussion below).

Bader's quantum theory of atoms in molecules provides the necessary formalism for assigning the effective charges to atoms.[12] These charges can be further broken down into contributions from the individual orbitals by considering the relevant atomic orbital overlap matrices.[9] We have performed such a population analysis for adducts **2** and **3** in order to further elucidate the role of a_1 ($\sigma \rightarrow \sigma^*$ donation), b_1 ($\pi \rightarrow \pi^*$ back-donation), and b_2 ($\sigma \rightarrow \pi^*$ back-donation) interactions in forming the borabenzene–ligand bonds. The results are presented in Table IV.

Table III. Analysis of the Electron Density in Borabenzene and Its Adducts with CO and N_2[a]

	free molecules	borabenzene adduct
B–C bond		
r_{B-Crit}		0.9163
ρ_{Crit}		0.1340
$\nabla^2\rho_{Crit}$		0.6416
ϵ		0.0410
C_4–O bond		
$r_{C4-Crit}$	0.6946	0.7013
ρ_{Crit}	0.4998	0.5035
$\nabla^2\rho_{Crit}$	1.7268	1.4514
ϵ	0.0000	0.0080
B–N_1 bond		
r_{B-Crit}		0.9403
ρ_{Crit}		0.0926
$\nabla^2\rho_{Crit}$		0.7257
ϵ		0.3621
N_1–N_2 bond		
$r_{N1-Crit}$	1.0183	1.0855
ρ_{Crit}	0.7108	0.6940
$\nabla^2\rho_{crit}$	−2.7533	−2.6234
ϵ	0.0000	0.0327

[a] All entries in atomic units. ϵ denotes the bond ellipticity.

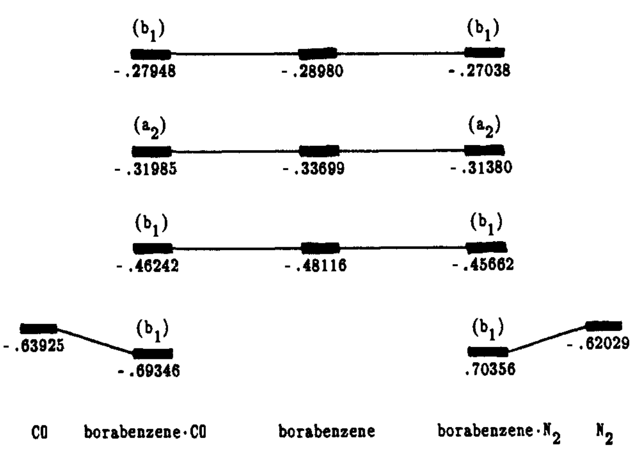

Figure 2. Schematic correlation diagram for the occupied π-orbitals in borabenzene and its adducts. Orbital energies are given in atomic units.

As expected, there is no significant a_2 interaction. However, the data in Table IV reveal a large $b_1(\pi)$ back-donation. In fact, the π-electron charge transfer has a greater magnitude than the σ-electron (a_1) one. This results in a net electron transfer *from* the borabenzene molecule to the CO or N_2 ligand. The b_2 back-donation is also pronounced, although its magnitude amounts to ca. 30% of the b_1 one. The results of Bader population analysis are quite unexpected, taking into account the presumed lack of π-electron back-donation as discussed above. The large π-electron charge transfer (as compared to the σ-electron one) is also at variance with the presence of a low-lying, strongly localized σ^* orbital of borabenzene (the orbital energy: $\epsilon = 0.10083$ au) and the higher energy of the π^* orbitals of the CO ($\epsilon = 0.16795$ au) and N_2 ($\epsilon = 0.18096$ au) molecules that are highly delocalized. Also, if one uses the differences of the orbital energies as a rough measure of the stabilization/destabilization effects, the combined a_2 and b_1 interactions destabilize the CO adduct by about 3 kcal/mol and stabilize the N_2 adduct by about 10 kcal/mol

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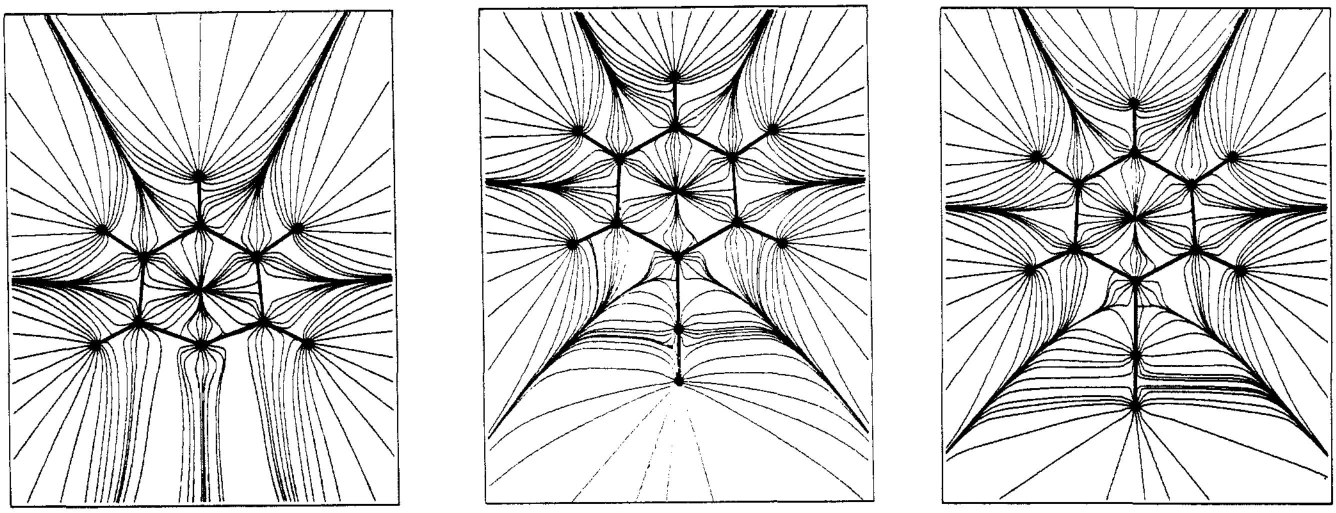

Figure 3. Gradient paths in borabenzene and its adducts in their molecular planes: (A, left) borabenzene (**1**), (B, middle) borabenzene·CO (**2**), (C, right) borabenzene·N_2 (**3**).

Table IV. Bader Atomic Electron Populations in Borabenzene Adducts and Free Molecules

	borabenzene·CO			borabenzene·N_2		
	C_4	O_1	total	N_1	N_2	total
free molecules						
a_1	4.085	5.915	10.000	5.000	5.000	10.000
b_2	0.258	1.742	2.000	1.000	1.000	2.000
a_2	0.000	0.000	0.000	0.000	0.000	0.000
b_1	0.258	1.742	2.000	1.000	1.000	2.000
total	4.601	9.399	14.000	7.000	7.000	14.000
adducts						
a_1	3.982	5.810	9.792	5.022	4.858	9.880
b_2	0.378	1.730	2.108	1.162	0.898	2.060
a_2	0.002	0.000	0.002	0.002	0.000	0.002
b_1	0.560	1.790	2.350	1.204	0.970	2.174
total	4.922	9.330	14.252	7.390	6.726	14.116
charge transfer[a]						
a_1	0.103	0.105	0.208	−0.022	0.142	0.120
b_2	−0.120	0.012	−0.108	−0.162	0.102	−0.060
a_2	−0.002	0.000	−0.002	−0.002	0.000	−0.002
b_1	−0.302	−0.048	−0.350	−0.204	0.030	−0.174
total	−0.321	0.069	−0.252	−0.390	0.274	−0.116

[a] A plus sign corresponds to the charge transfer from the borabenzene moiety.

(Figure 2). This means that, at least in **2**, the π interactions play only a secondary role.

There is a plausible explanation of this underestimation of the σ donation and exaggeration of the π back-donation within the Bader analysis. The calculated charge transfer for the N_1 atom in **3** provides the first clue (Table IV). There is a small σ-electron charge transfer *from* the borabenzene molecule! The gradient maps (Figure 3) are also helpful. Two characteristic features are present: First, the atomic basin of the boron atom in **1** has a very narrow opening angle. Second, the critical points in **2** and **3** (and the positions of the atomic boundaries) are very close to the boron atom. As revealed in Table IV, the boron atom-critical point distance ($r_{\text{B-Crit}}$) constitutes only about 30% of the bond length.

When a new bond is formed three distinct phenomena occur: There is a charge transfer from one fragment to the other. There is a polarization of the fragments which results in induction of dipole moments. The third effect, which is inherent to the quantum theory of atoms in molecules, is a formation of a new atomic boundary. The changes in atomic populations arise from both charge transfer and the altered shapes of atomic basins as the integration domains for the individual atoms change. It is usually presumed that these two contributions are somehow proportional. In **2** and **3**, however, the atomic basin of the boron atom shrinks dramatically upon formation of the adducts. The net effect is a formal additional acquisition of the negative electric charge by the atoms C_4 in **2** and N_1 in **3**. This translates into the calculated smaller σ donation to and larger π back-donation from the borabenzene molecule than it would be if only the genuine charge-transfer effects were considered.

Table V. GAPT Atomic Charges in Borabenzene and Its Adducts with CO and N_2

	free molecules	borabenzene·CO	borabenzene·N_2
C_5H_5B			
B	0.374	−0.471	0.016
C_1	−0.339	−0.011	−0.178
C_2	0.221	−0.045	0.090
C_3	−0.373	−0.042	−0.201
H_1	0.093	0.013	0.021
H_2	0.012	0.000	−0.007
H_3	0.025	0.004	0.002
CO			
C_4	0.361	1.670	
O	−0.361	−1.074	
N_2			
N_1	0.000		0.668
N_2	0.000		−0.338
ΔQ[a]		0.596	0.330

[a] A plus sign corresponds to the charge transfer from the borabenzene moiety.

Another formal look at the electron distribution in **1**, **2**, and **3** is provided by the GAPT atomic charges.[10] The results are given in Table V. In the borabenzene molecule the GAPT analysis results in a pattern of alternating positive and negative charges. This is a nice illustration of a general rule which says that upon a single-site perturbation of a carbon backbone each second atom acquires a charge of the same sign.[14] As expected, the boron atom in **1** bears a positive charge. According to the GAPT analysis, upon formation of both **2** and **3** a net electron transfer (ΔQ in Table V) to the borabenzene moiety occurs. The magnitude of this transfer in **2** is roughly twice as much as in **3**, which is in agreement with the relative stabilities and respective force constants for the B–C_4 and B–N_1 bonds (Table II). In the CO adduct, the major part of the electric charge is localized within the B–C_4–O moiety. For the sake of comparison we also list here the Bader and GAPT magnitudes of charge transfer for the BH_3·CO complex. They are −0.083 and 0.2522, respectively.

Although we have not calculated either Bader or GAPT atomic charges for the MP2 wave function, we anticipate that inclusion of electron correlation would result in reduction of the magnitudes of the calculated charges. This prediction stems from the general observations already published in chemical literature.[10,15,16]

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Final comment should be devoted to the calculated vibrational frequencies. At the HF/6-31G* level, the shift in the frequency of the N–N stretching in **3** is $\Delta\nu = -51$ cm^{-1} compared to the N_2 molecule. The reported experimental value is $\Delta\nu = -133$ cm^{-1}.[3] We believe that inclusion of the electron correlation is necessary to obtain a reasonable agreement for $\Delta\nu$. For the CO adduct, the calculations yield $\Delta\nu = -42$ cm^{-1}.

Conclusions

The results of HF/6-31G* and MP2/6-31G* calculations demonstrate high reactivity of the borabenzene molecule toward carbon monoxide and nitrogen. The adduct formed between borabenzene and carbon monoxide exhibits a remarkable stability. The nitrogen adduct, though less stable, should be isolable. The reactivity of borabenzene can be attributed to a donation from the nonbonding σ^0 orbital of either CO or N_2 to the low-lying vacant σ^* orbital of borabenzene. Relief of the strain within the borabenzene ring can further contribute to the exothermicity of the addition reactions. The charge distribution in both free borabenzene and its adducts seems to be better rationalized within the GAPT population analysis than the Bader one.

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Ab Initio SCF MO and Natural Bond Orbital Studies of 7-Silanorbornadiene and 7,7-Dimethyl-7-silanorbornadiene. Two Molecules Possessing an Inverted Sequence of π Orbitals

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Abstract: The geometries of norbornadiene, **1**, 7-silanorbornadiene, **2**, and 7,7-dimethyl-7-silanorbornadiene, **3**, have been optimized at the HF/STO-3G and HF/3-21G levels (within C_{2v} symmetry constraint). In addition, **2** has also been optimized by using the 3-21G(*) basis set which contains a set of polarization functions on Si. It was found that, although the π canonical MOs (CMOs) of **1** followed the natural sequence, i.e., π_+ (a_1) below π_- (b_1), the inverted sequence is observed (i.e., π_+ above π_-) for both **2** and **3**. Through-bond (TB) orbital interactions are therefore more important than through-space (TS) orbital interactions in **2** and **3**. The π^* CMOs, on the other hand, followed the natural sequence in all three molecules. Orbital interactions in **1** and **2** were dissected into TS and TB components by using the Weinhold natural bond orbital (NBO) localization procedure. It is found that TS interactions are weaker in **2** than in **1**, owing to the former molecule having a larger dihedral angle (120°) for the six-membered ring compared to **1** (114°). In addition, TB coupling to the π_+ orbital (which raises that level) is substantially larger in **2** than in **1**, an effect that is attributed to the more electropositive nature of silicon compared to carbon. The combination of weakened TS interactions and strengthened TB interactions is sufficient to cause the inverted sequence of π levels in **2** (and in **3**). TB and TS effects are found to reinforce each other in the π^* manifolds of both **1** and **2**; consequently, an inverted sequence of π^* levels is unlikely to be found in any type of simple norbornadiene molecule. The NBO analysis of interactions in the π manifold showed that σ/π interactions dominate over σ^*/π interactions. However, both σ^*/π^* and σ/π^* interactions should be considered in the analysis of TB coupling in the π^* manifold, with the former being slightly larger than the latter.

Recent experimental studies[1] have demonstrated the occurrence of unusually rapid intramolecular electron transfer between donor and acceptor groups fixed at predetermined distances, by rigid polynorbornyl spacers. Such rapid rates were attributed to a strong through-bond coupling mechanism between the donor and acceptor orbitals with those of the polynorbornyl framework.[1e] In order to obtain a more detailed understanding of the coupling factor which is responsible for these large rates, we have undertaken both experimental and theoretical investigations of a series of model dienes with the two double bonds separated by norbornylogous spacer groups. Particular emphasis has been placed on the splittings between the π cation and between the π^* anion states of these compounds. These splittings, which provide a measure of the electronic coupling between the donor and acceptor groups (both ethylenic in the model compounds), figure prominently in the theory of electron transfer. In the present work, we examine in detail the simplest member of this series of model compounds, norbornadiene, **1**, and consider as well 7-silanorbornadiene, **2**, and 7,7-dimethyl-7-silanorbornadiene, **3**. Specifically, we explore the utility of localized orbital methods for analyzing the contributions of through-bond (TB) and through-space (TS) interactions to the splittings between the π cation and between the π^* anion states.[2]

Norbornadiene **1** has become a paradigm for a molecule that exhibits dominant through-space (TS) orbital interactions within both π and π^* manifolds.[2-8] This is a consequence of the structurally enforced propinquity of the double bonds in **1** (they

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