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Watson-Crick Base Pairs with Thiocarbonyl Groups: How Sulfur Changes the Hydrogen Bonds in DNA

Invited paper

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Abstract: We have theoretically analyzed mimics of Watson-Crick AT and GC base pairs in which N–H•••O hydrogen bonds are replaced by N–H•••S, using the generalized gradient approximation (GGA) of density functional theory at BP86/TZ2P level. The general effect of the above substitutions is an elongation and a slight weakening of the hydrogen bonds that hold together the base pairs. However, the precise effects depend on how many, and in particular, on which hydrogen bonds AT and GC are substituted.. Another purpose of this work is to clarify the relative importance of electrostatic attraction *versus* orbital interaction in the hydrogen bonds involved in the mimics, using a quantitative bond energy decomposition scheme. At variance with widespread believe, the orbital interaction component in these hydrogen bonds is found to contribute more than 40% of the attractive interactions and is thus of the same order of magnitude as the electrostatic component, which provides the remaining attraction.

Keywords: *Chitosan Density functional calculations • DNA structures • Sulfur • Hydrogen bonds • Watson-Crick pair mimics*

1. Introduction

Chemically modified DNA bases, such as thioguanine, and thiouracil are of interest because of their pharmacological capabilities. [1-3] Thioguanine, which is used in the therapy of acute leukemia, is believed to exert its cytotoxic therapeutic effect by being incorporated into DNA as deoxy-6-thioguanosine. [4,5] Because of their therapeutic relevance, these modified bases have also been the subject of theoretical studies. [6-8].

The Watson-Crick DNA base pairs have been extensively studied with ab initio theory. [9-19] In our previous work, [20-25] we showed that the generalized gradient approximation (GGA) of density functional theory (DFT) is an efficient alternative to conventional ab initio theory for accurately describing the hydrogen bonds involved in Watson-Crick base pairs (AT and GC, see Scheme 1) and in the weakly bound water dimer. [21] Our bond analyses in the frame of Kohn-Sham DFT [26] revealed that the contribution of occupied–virtual orbital interactions to the Watson-Crick hydrogen bonds is of the same order of magnitude as electrostatic interactions. [20-25] The orbital interaction component mostly originates from donor–acceptor interactions of lone pairs on nitrogen and oxygen atoms of one DNA base with empty N–H σ^* orbitals of the other base. [20,21,23] Very recently, we found that, at variance with widespread believe, [27-31] such an orbital interaction component is prominent even in rather weakly bound base pairs, such as those of adenine (A) with 2,4-difluorotoluene (F), a mimic of thymine (T), and of fluorine-substituted mimics of G and C, respectively. [32-35] In these systems, the oxygen atoms are replaced by the poorer proton-acceptor fluorine and the N1–H1 of guanine is replaced by the poorer proton-donor C–H (see also Scheme 1).

These findings raise an important question: are these isolated examples, or is the occurrence of a significant orbital-interaction component in hydrogen bonds a more general phenomenon?

In the present study, we tackle the above question by extending our analyses to a series of 6 mimics of

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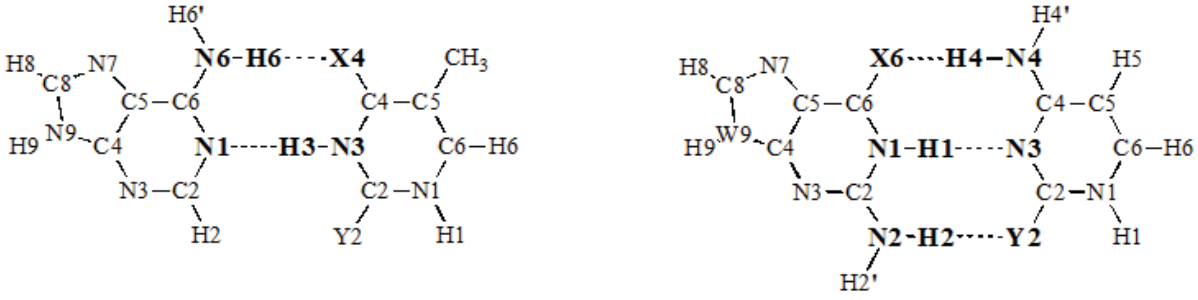

Scheme 1. Model systems of this investigation: AT and GC Watson-Crick pairs and mimics thereof in which C=O in T, G and C have been replaced by C=S (X, Y = O, S).

Watson-Crick AT and GC base pairs in which N–H•••O hydrogen bond is replaced by N–H•••S, respectively (see Scheme 1). We explore how the effects on structures and energies depend on how many and, in particular, on which hydrogen bonds are substituted in AT and GC. Another purpose is the elucidation of the hydrogen-bonding mechanism, in particular, the relative importance of frontier-orbital interactions and electrostatic attraction. This is done in the conceptual framework provided by the Kohn-Sham molecular orbital model using a quantitative bond energy decomposition scheme (*vide infra*). [26]

2. Theoretical Methods

2.1. General Procedure

All calculations were performed using the Amsterdam Density Functional (ADF) program developed by Baerends and others [36-52] and QUILD, an adapted version of ADF, developed by Swart and Bickelhaupt. [53] The numerical integration was performed using the procedure developed by te Velde *et al*. [42,43] The MOs were expanded in a large uncontracted set of Slater type orbitals (STOs) containing diffuse functions: TZ2P (no Gaussian functions are involved). [44] The basis set is of triple-ζ quality for all atoms and has been augmented with two sets of polarization functions, i.e. 3d and 4f on C, N, O, S and 2p and 3d on H. The 1s core shell of carbon, nitrogen, and oxygen and the 2p core shell of sulfur were treated by the frozen-core approximation.[38] An auxiliary set of s, p, d, f and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field cycle. [45]

Equilibrium structures were optimized using analytical gradient techniques. [46] Geometries and energies were calculated at the BP86 level of the generalized gradient approximation (GGA): exchange is described by Slater's Xα potential [47] with corrections due to Becke [48,49] added self-consistently and correlation is treated in the Vosko-Wilk-Nusair (VWN) parameterization [50] with nonlocal corrections due to Perdew [51] added, again, self-consistently (BP86). [52] Energy minima have been verified to be equilibrium structures through vibrational analyses. All species were found to have zero imaginairy frequencies, except for GC_s, which has a very small imaginary frequency of *i* 18.7 cm^{-1}. This small imaginary frequency, however, was shown to be spurious using an explicit potential-energy scan.

2.2. Bonding Energy Analysis

The overall bond energy ΔE is made up of two major components (eq 1).

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \quad (1)$$

In this formula, the preparation energy ΔE_{prep} is the amount of energy required to deform the separate bases from their equilibrium structure to the geometry that they acquire in the pair. The interaction energy ΔE_{int} corresponds to the actual energy change when the prepared bases are combined to form the base pair. It is analyzed in the hydrogen-bonded model systems in the framework of the Kohn-Sham MO model using a decomposition of the bond energy into electrostatic interaction, exchange repulsion (or Pauli repulsion), and (attractive) orbital interactions (eq 2). [26,54,55]

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} \quad (2)$$

The term ΔV_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared (i.e. deformed) bases and is usually attractive. The Pauli-repulsion ΔE_{Pauli} comprises the destabilizing interactions between occupied orbitals

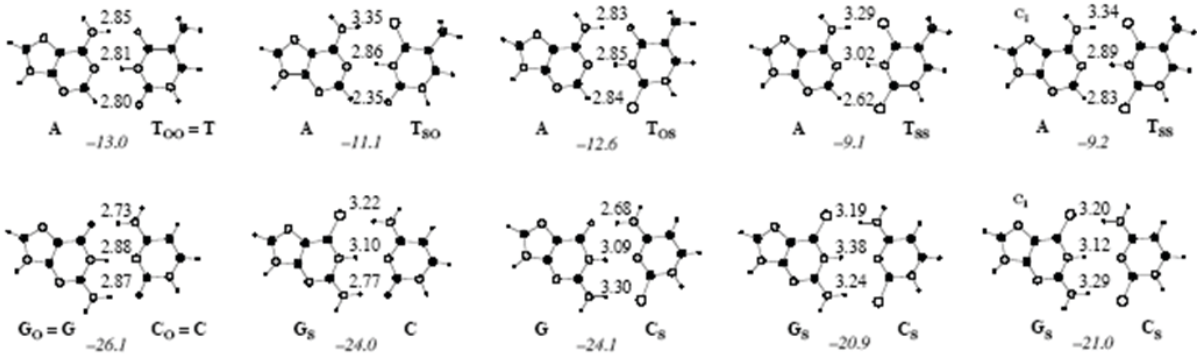

Figure 1. N6–X4, N1–N3 and H2–Y2 distance (in Å) in the Watson-Crick AT pair, the X6–N4, N1–N3 and N2–Y2 distances (in Å) in the Watson-Crick GC pair and artificial mimics of both pairs computed at BP86/TZ2P (see Scheme 1). Bond energies (in kcal/mol) are given in italics below base pairs (for BSSE corrections, see Table 1). The double substituted mimics are given in C_S and C_1 symmetry.

and is responsible for the steric repulsion. The orbital interaction ΔE_{oi} in any MO model, and therefore also in Kohn-Sham theory, accounts for charge transfer (*i.e.*, donor–acceptor interactions between occupied orbitals on one moiety with unoccupied orbitals of the other, including the HOMO-LUMO interactions) and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment). Since the Kohn-Sham MO method of DFT in principle yields exact energies, and in practice, with the available density functionals for exchange and correlation, rather accurate hydrogen-bond energies, we have the special situation that a seemingly one-particle model (a MO method) in principle completely accounts for the bonding energy. In particular, the orbital-interaction term of the Kohn-Sham theory comprises the often distinguished attractive contributions charge transfer, induction (polarization) and dispersion, although the extent to which the latter is contained in practical implementations such as GGA is not well defined (for more details, see Ref. [34]).

The orbital interaction energy can be decomposed into the contributions from each irreducible representation Γ of the interacting system (eq 3) using the extended transition state (ETS) scheme developed by Ziegler and Rauk [56-58] (note that our approach differs in this respect from the Morokuma scheme, [54,55] which instead attempts a decomposition of the orbital interactions into polarization and charge transfer). In systems with a clear σ, π, or A', A" separation (such as our DNA bases), this symmetry partitioning proves to be most informative.

$$\Delta E_{oi} = \sum_{\Gamma} \Delta E_{\Gamma} \qquad (3)$$

2.3. Analysis of the Charge Distribution

The electron density distribution is analyzed using the Voronoi deformation density (VDD) method introduced in Ref. [59]. The VDD charge Q_A is computed as the (numerical) integral of the deformation density $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \Sigma_B \rho_B(\mathbf{r})$ associated with the formation of the molecule from its atoms in the volume of the Voronoi cell of atom A (eq 4). The Voronoi cell of atom A [43,60] is defined as the compartment of space bound by the bond midplanes on and perpendicular to all bond axes between nucleus A and its neighboring nuclei (cf. the Wigner-Seitz cells in crystals).

$$Q_A = -\int_{\text{Voronoi cell A}} \left(\rho(r) - \sum\nolimits_B \rho_B(r)\right) dr \qquad (4)$$

Here, $\rho(\mathbf{r})$ is the electron density of the molecule and $\Sigma_B \rho_B(\mathbf{r})$ the superposition of atomic densities ρ_B of a fictitious promolecule without chemical interactions that is associated with the situation in which all atoms are neutral. The interpretation of the VDD charge Q_A is rather straightforward and transparent. Instead of measuring the amount of charge associated with a particular atom A, Q_A directly monitors how much charge flows, due to chemical interactions, out of ($Q_A > 0$) or into ($Q_A < 0$) the Voronoi cell of atom A, that is, the region of space that is closer to nucleus A than to any other nucleus.

3. Results and Discussion

3.1. Assessment of the Approach

The choice of the BP86 density functional [48-51] and the TZ2P basis set is based on our previous investigation [21,61] of the performance of various GGA density functionals and basis sets for the AT and GC Watson-Crick base pairs in which it was shown that the BP86/TZ2P agrees excellently with experiment [62] and

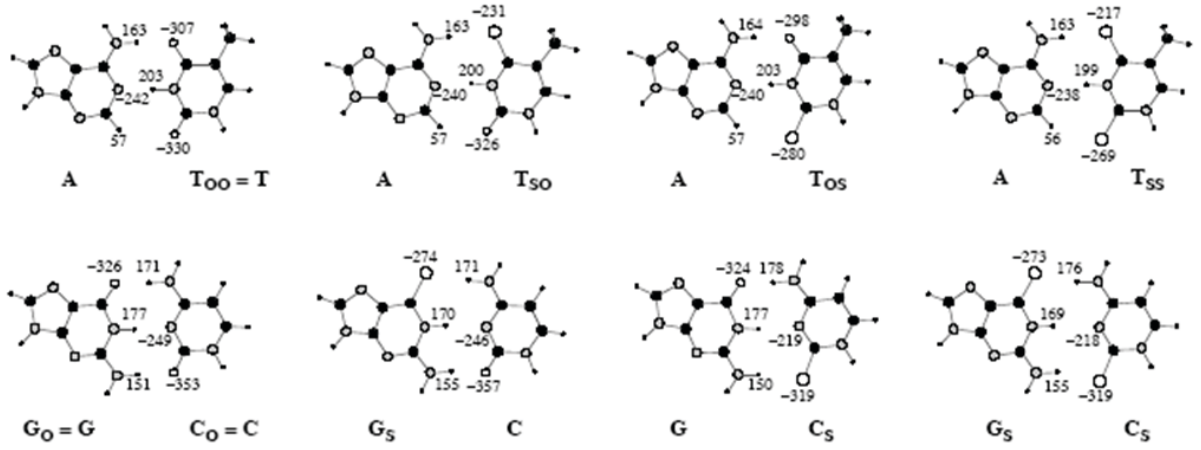

Figure 2. VDD atomic charges (in mili-electrons) of the isolated bases adenine, thymine, guanine, cytosine and sulfur mimics thereof. Bases were calculated in the geometry that they acquire in the indicated base pair.

ab initio calculations. [9-19] This was also confirmed in a more recent study on mismatches of DNA bases. [23] In the present study we have optimized all systems in C_s (see Fig. 1 and Table 1) and the double substituted systems also in C_1 symmetry (shown in Fig. 1 and Table 1). All C_s geometries of the single substituted base pairs and the C_1 geometries of the double substituted geometries have been verified to be true minima with frequency analysis. Table 1 also contains ab initio hydrogen bond energies, [6-8] which are in agreement with our BP86 energies. For all pairs the BSSE correction was between 0.6 and 0.9 kcal/mol (see Table 1)

3.2. Effect of substituting oxygen by sulfur in AT

The effect of replacing the N–H•••O hydrogen bond in natural Watson-Crick base pairs by N–H•••S is a slight weakening of the interaction energy and an elongation of the hydrogen bonds. Substitution of the O4 of thymine in the AT base pair by a sulfur atom leads to an elongation of the N6–X4 hydrogen bond from 2.85 to 3.35 Å due to the larger size of the sulfur atom (see Scheme 1 and Fig. 1). This expansion of N6–X4 also forces the N1–N3 bond to expand by 0.05 Å. As a consequence, the distance between H2 and O2 is compressed from 2.80 to 2.35 Å. The hydrogen bond energy decreases only slightly from –13.0 for natural AT (i.e., AT_{OO}) to –11.1 for AT_{SO} (see Scheme 1 and Fig. 1).

Note that O2 in thymine is not involved in hydrogen bonding (see Scheme 1). Previously, we have shown that it has a slightly destabilizing interaction with the C2–H2 bond in adenine [23] and that substituting it by the smaller fluorine atom has no effect on the hydrogen bonds of the AT mimic. [32-35]

In nice agreement with these previous results, substitution of the O2 of thymine by the sterically more demanding sulfur atom leads to an elongation of the distance between H2 and Y2 from 2.80 to 2.84 Å and a slight weakening of the hydrogen-bond strength by 0.4 kcal/mol (see Fig. 1). Note also that this has an immediate effect of forcing the N1–N3 hydrogen bond to expand and the N6–O4 hydrogen bond to compress from 2.85 to 2.83 Å (see Fig. 1).

When both oxygen atoms of thymine are substituted, the base pair is no longer flat: instead, the bases become propeller-like twisted around the N1–N3 bond. The dihedral angle ∠S4-N6-N1-N3 is 30.6°. A comparison of the C_S and C_1 geometry of AT_{SS} shows that the energy difference between the two geometries is very small, only 0.1 kcal/mol (see Fig. 1). However, the AT_{SS} systems prefers the propeller-twisted geometry because, in this way, it can shorten the N1–N3 hydrogen bond from 3.02Å in C_S to 2.89Å in C_1 symmetry. This is achieved at the expense of the ∠N6-H6-S4 hydrogen-bond angle, which goes from 179.5° in C_S symmetry to 170.0° in C_1 symmetry. The amino group is pyramidal in C_1 symmetry.

3.3. Effect of substituting oxygen by sulfur in GC

In the case of GC, the effect of replacing N–H•••O by N–H•••S is a reduction in bond energy of approximately 2 kcal/mol for the first substitution and 5.1 kcal/mol when both outer hydrogen bonds are substituted. The effects of elongation and compression are similar to those found for AT (*vide supra*). When the oxygen in the upper hydrogen bond is replaced, i.e., O6 in guanine becomes S6 (see Scheme 1), this hydrogen bond X6–N4 expands from 2.73 to 3.22 Å, together with the middle hydrogen bond N1–N3 which expands from 2.88 to 3.10 Å (see Fig. 1). Thus, the lower hydrogen bond *contracts* by 0.1 Å (see Fig. 1).

However, when the oxygen atom in the lower hydrogen bond is replaced, i.e., O2 in cytosine becomes

Table 1. Analysis of the base–base interaction energy (in kcal/mol) in the Watson-Crick AT and GC pairs and mimics thereof.[a]

	AT	AT_{SO}	AT_{OS}	AT_{SS}	GC	G_SC	GC_S	G_SC_S
ΔE_{Pauli}	38.7	33.7	38.6	33.1	51.9	42.9	45.4	37.8
ΔV_{elstat}	–31.8	–27.5	–31.7	–25.9	–48.5	–41.2	–42.7	–34.9
$\Delta E_{Pauli} + \Delta V_{elstat}$	6.9	6.2	6.9	7.3	3.4	1.7	2.7	2.9
ΔE_{σ}	–20.4	–18.0	–20.1		–29.2	–25.5	–26.7	
ΔE_{π}	–1.7	–1.3	–1.6		–4.8	–4.3	–4.5	
ΔE_{oi}	–22.1	–19.3	–21.8	–18.7	–34.0	–29.8	–31.1	–27.4
ΔE_{int}	–15.2	–13.2	–14.9	–11.5	–30.6	–28.1	–28.4	–24.5
ΔE_{prep}	2.2	2.1	2.3	2.3	4.5	4.1	4.3	3.7
ΔE (C_s)	–13.0	–11.1	–12.6		–26.1	–24.0	–24.1	–21.0
ΔE (C_1)				–9.2				
ΔE (BSSE corrected)	–12.3	–10.4	–11.9	–8.6	–25.2	–23.2	–23.4	–20.3
% ΔE_{oi} in ($\Delta E_{oi} + \Delta V_{elstat}$)	41%	41%	41%	42%	41%	42%	42%	44%
MP2/6-31+G(2d',p')//HF/6-31G(d,p)[b]	–13.1	–11.6	–12.9		–26.1	–23.5	–23.6	
MP2/6-31G*(0.25)//HF6-31G*[c]		–11.2	–12.1			–22.5		

[a] *Computed at BP86/TZ2P. The mono-substituted mimics were calculated in C_S symmetry and the double-substituted mimics in C_1 symmetry. All species are equilibrium structures.*
[b] *Work by Kawahara et al. [7]. They used substituted uracil instead of thymine, which affects the A-T bond strength ΔE by only 0.1 kcal/mol [63].*
[c] *Work by Sponer et al. [6]. They used substituted uracil instead of thymine, which affects the A-T bond strength ΔE by only 0.1 kcal/mol [63].*

S2 (see Scheme 1), the N2–Y2 distance elongates from 2.87 to 3.30 Å, the middle hydrogen bond enlarges by 0.21 Å. Consequently, the upper hydrogen bond O2–N4 is compressed from 2.73 to 2.68 Å (see Fig. 1).

Substitution of both oxygen atoms in the GC pair by sulfur atoms leads, as in AT, to a non-planar system with pyramidal amino groups (see G_SC_S in Fig. 1). The G_SC_S system prefers a propeller-twisted geometry around the N1–N3 hydrogen bond to shorten the N1–N3 bond from 3.38Å in the flat geometry to 3.12Å in the non-planar geometry. The dihedral angle ∠ S6-N4-N3-N1 is 31.2°. The other two hydrogen bonds can adapt to the twisted situation, i.e., stay oriented towards the sulfur atoms, by pyramidalizing the amino group on both bases.

3.4. Atomic Voronoi Deformation Density atomic charges

In our previous work, [23] we have established with the VDD atomic charges that the DNA bases are electronically complementary and that they posses the right charge distribution for achieving a favorable electrostatic interaction in the base pairs. Here, we examine for the sulfur mimics of the DNA bases how the VDD atomic charge of the front atoms is influenced if oxygen is substituted by sulfur. The VDD atomic charges of the front atoms are given in Fig. 2 for the *isolated* bases *in the geometry that they acquire in the base pair*. Therefore, the small differences in atomic charges between adenine in the different base pairs are due to the slightly different geometry of this base in the different base pairs. The substitution of oxygen by sulfur always leads to a decrease of electronic charge of that front atom by up to 0.09 electrons (see Fig. 2). However, a negligible effect is seen on the other front atoms due to the substitution. Thus, the sulfur atom in the sulfur substituted DNA-base mimics is less negatively charged than the oxygen atom in the natural bases, in line with its smaller electronegativity.

3.5. Nature of the Hydrogen Bonds in Sulfur substituted Watson-Crick base pairs

We find that hydrogen bonding receives an important stabilizing contribution from occupied-virtual orbital interactions, which are in the same order of magnitude as electrostatic interaction. Interestingly, this is so also in the sulfur-substituted mimics involving N–H•••S hydrogen bond, and not only in natural Watson-Crick pairs with the N–H•••O hydrogen bonds for which the importance of orbital interactions was already shown in earlier work [20-24]. Our evidence is summarized in Table 1 showing the percentage contribution of the orbital interactions ΔE_{oi} to all bonding forces (i.e., ΔE_{oi} + ΔV_{elstat}) between the bases in Watson-Crick AT and GC pairs and the sulfur mimics thereof. From the contribution of ΔE_{oi}, we see that substitution of oxygen as a H-bond acceptor by sulfur does essentially not change the percentage of somewhat more than 40%. Thus, the orbital interactions remain important in both types of Watson-Crick hydrogen bonds.

4. Conclusions

Substitution of O by S in N–H•••O hydrogen bonds in AT and GC Watson-Crick pairs causes hydrogen bonds to slightly weaken and to elongate. The singly substituted base pairs remain flat, whereas the doubly substituted base pairs become propeller-like twisted. This follows from our theoretical analyses at BP86/TZ2P of AT and GC Watson-Crick pairs and 6 mimics thereof in which various combinations of the above substitutions have been applied.

Interestingly, the formally nonbonded C2–H2•••O2 contact in AT (i.e., AT_{OO}) is found to turn into a clearly (although not strongly) repulsive, destabilizing contact if the O2 oxygen is replaced by a sterically more demanding sulfur atom in AT_{OS} and AT_{SS} (see Scheme 1).

Furthermore, we find that the hydrogen bonds between the modified bases are still to an important extent provided by occupied–virtual orbital interactions, and not only by electrostatic attraction. The orbital interaction term accounts for more than 40% of all attractive forces; the remaining attraction stems from classical electrostatic interaction.

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Supporting Information

Cartesian coordinates of all sulfur-substituted DNA base pairs in this study are available upon request from the authors.

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