

Polyacene and Cyclacene Geometries and Electronic Structures: Bond Equalization, Vanishing Band Gaps, and Triplet Ground States Contrast with Polyacetylene

K. N. Houk,* Patrick S. Lee, and Maja Nendel

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

houk@chem.ucla.edu

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The ground-state geometries and excited singlet and lowest triplet energies of polyacenes from benzene through nonacene are predicted with B3LYP/6-31G* calculations and compared to experimental data where available. The results are compared to these data for cyclacenes and polyenes. The polyacenes and cyclacenes have geometries consisting of two fully delocalized nonalternating ribbons joined by relatively long bonds. Polyacenes are predicted to have smaller band gaps than the corresponding polyenes and triplet ground states for nine or more benzene rings. The fully delocalized nonalternating nature of polyacenes differs from the bond alternation resulting from Peierls distortion in polyenes. The differences are rationalized in terms of a simple MO model, and the results are compared to extensive prior theoretical work in the literature. Predictions about the electronic structure of analogues containing polyacene units are made.

Introduction

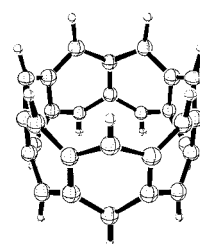
Cyclacenes **1** (Chart 1) are hypothetical substances that form the basic cylindrical carbon units of one type of nanotube.¹ Synthetic attempts have failed to yield a monomeric cyclacene,² but theoretical interest has been high in the electronic properties, geometries, and stabilities of such substances.³

A recent report included a prediction that the aromaticity of each of the benzene rings in cyclacenes with 5–14 benzene rings was reduced by the strain of the cyclic system.³ These cyclacenes no longer have aromatic bond lengths, but rather structures resembling two weakly interacting Schleyer “trannulenes”,⁴ which are circular, all-trans cyclic polyene ribbons. Recently, Türker has explored cyclacenes with AM1, but he mainly discussed the MOs as a function of size.⁵

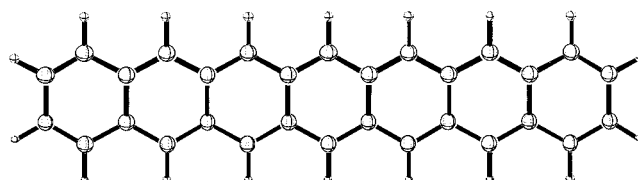
Polyacenes, linear polybenzenoid hydrocarbons, are acyclic variants of cyclacenes. Representative substances of this type, such as pentacene, have proven to have remarkable properties and have been incorporated into several types of organic electronic devices.⁶ The electronic structures of polyacenes have been discussed extensively in the literature.^{7–10} It has been proposed that polyacenes would have properties differing from polyacetylenes.^{7,8}

Band theory arguments proposed by Kertesz and Hoffmann⁷ and by Chapman and Kivelson⁸ showed that superconductivity could arise from the unusually small band gaps in polyacenes. While arguments for and

Chart 1

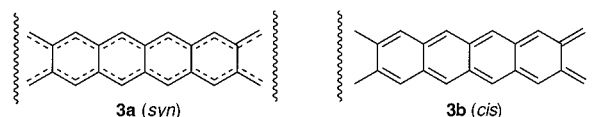


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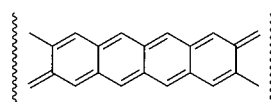
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against the symmetrical (**3a**) or cis and trans distorted (**3b** and **3c**) structures have been made, valence-bond arguments place all of these close in energy, with **3a** lowest.¹⁰ Low band gaps have been predicted,^{7–10} but whether a triplet ground state is feasible seems not to have been considered.



3a (syn)

3b (cis)



3c (trans)

We report a theoretical comparison between cyclacenes and acyclic linear polyacenes and polyenes and identify

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Table 1. Predicted Singlet–Singlet (S_0 – S_1) and Singlet–Triplet (S_0 – T_1) Energy Gaps (eV)

n^a	polyene ^b S_0 – T_1	polyene ^c S_0 – S_1	polyacene ^b S_0 – T_1	polyacene ^c S_0 – S_1	cyclacene ^b S_0 – T_1
1	3.58	8.47	3.88	5.54	
2	2.53	6.04	2.71	4.46	
3	1.92	4.87	1.81	3.28	
4	1.54	4.14	1.20	2.49	
5	1.28	3.63	0.78	1.95	0.56
6	1.10	3.25	0.46	1.54	–0.05
7	0.96	2.96	0.24	1.24	0.36
8	0.85	2.72	0.07	1.00	0.04
9	0.76	2.53		0.80	0.03
10	0.69	2.36			0.07
11	0.63	2.16			–0.16
12	0.58	2.00			0.10
13	0.54	1.85			–0.30
14					0.11

^a n = number of double bonds in a polyene or the number of benzene rings in a polyacene or cycloacene. ^b B3LYP/6-31G* for S_0 , UB3LYP/6-31G* for T_1 . ^c TDDFT.

properties common to both cyclacenes such as **1** and linear polyacenes such as **2**. We find that both cyclacenes and polyacenes resemble parallel weakly interacting trannulenes. A simple molecular orbital model is presented that rationalizes the unusual geometries of both of these systems and the apparent deviations from expectation based upon Peierls instabilities. The arguments are related to each bond theory consideration.^{7,8} The potential for novel electronic properties of such substances proposed first by Kivelson and Chapman⁶ is confirmed by these quantitative density functional theory quantum mechanical calculations. Polyacenes above octacene are predicted to have triplet ground states, a feature related to the extreme reactivity of such species.⁷

Theoretical Methods

The B3LYP hybrid density functional method with the 6-31G* basis set was used to compute the geometries and energies reported here.¹¹ The program GAUSSIAN 98 was used throughout.¹² UB3LYP was used for calculations on triplets. Band gaps, which are equal to S_0 – S_1 transition energies, were computed with TDDFT methods.¹² The S_0 – S_1 and S_0 – T_1 energy gaps for all the molecules studied here are given in Table 1 and plotted in Figure 3.

Results and Discussion

B3LYP calculations provide excellent geometries for small polyacenes as compared to experimental geometries: computed bond lengths are within 0.01 Å of the values obtained by X-ray crystallographic studies¹¹ of benzene, naphthalene, anthracene, tetracene, and pentacene.¹² Two examples are shown in Figure 1.

Electronic properties are also reproduced adequately: for example, the experimental or estimated singlet–triplet gaps for the smaller polyacenes, benzene through hexacene, range from 85 to 12 kcal/mol, respectively,¹⁵ while B3LYP/6-31G* calculations predict 84–11 kcal/mol.

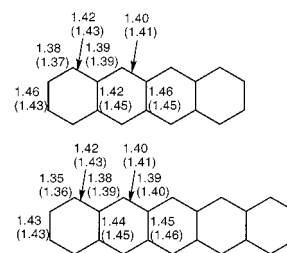
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**Figure 1.** Experimental and B3LYP/6-31G* (in parentheses) bond lengths of tetracene and pentacene.**Table 2. Experimental and Computed Adiabatic S_0 – T_1 and Vertical S_0 – S_1 Energies of Polyacenes**

n	experimental S_0 – T_1 (kcal/mol)	UB3LYP/ 6-31G* S_0 – T_1 (kcal/mol)	experimental S_0 – S_1 (eV) (nm)	TDDFT/ 6-31G* S_0 – S_1 (eV)
1	85	84	4.84 [256]	5.54
2	61	59	3.97 [312]	4.46
3	42	42	3.35 [370]	3.28
4	30	26	2.61 [475]	2.49
5	20	16	2.14 [582]	1.95
6	12	11	1.79 [695]	1.54

The available experimental results are compared to theory in Table 2. The agreement is within 4 kcal/mol (0.2 eV) for these molecules.

As shown in Table 2, the experimental vertical S_0 – S_1 transition energies for benzene through hexacene range from 4.84 eV (256 nm) to 1.79 eV (695 nm), while TDDFT (B3LYP/6-31G*) predicts values of 5.54–1.54 eV.¹⁵ With this small basis set, the transition energies are overestimated for the small systems but underestimated for the larger systems by 0.2–0.3 eV. The polyenes were also explored (Table 1), and some of these molecules were studied recently with TDDFT and a variety of basis sets.¹⁶

Turning to a comparison of the geometries of polyacenes and cyclacenes, we summarize the computed geometries of these species by the average structures shown in Figure 2. The cyclacene geometries are only slightly different from those of the linear polyacenes.¹⁷ Strain resulting from curvature of the cyclacenes has essentially no effect on the geometries, contrary to

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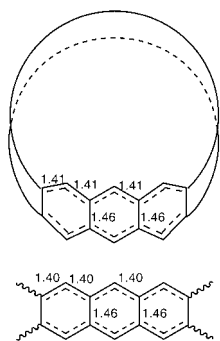
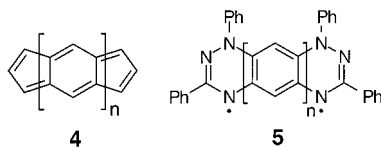


Figure 2. Average bond lengths of cyclacenes and polyacenes.

previous suggestions.³ The peripheral bonds of the cyclacene series range from 1.4 to 1.42 Å; the average length of these bonds is 1.41 Å. The bonds spanning each six-membered ring are between 1.45 and 1.47 Å in length, averaging 1.46 Å. In the linear polyacene series, neglecting the terminal benzene rings, the peripheral bonds range from 1.39 to 1.41 Å, averaging 1.40 Å, and the cross-ring bonds are in the range of 1.45–1.47 Å, averaging 1.46 Å (Figure 2). In both the linear polyacenes and the cyclacenes, the peripheral bonds form two parallel, delocalized polyacetylenic ribbons, with Pauling bond orders of 1.5. Polyacenes, like cyclacenes, resemble Schleyer's trannulenes.⁴ Extrapolating, larger polyacene systems would have 1.40 Å peripheral bonds and 1.46 Å cross-ring bonds. These values are essentially the same as found by Choi and Kim for cyclacenes.³ Our results show, however, that there is essentially no difference between polyacene and cyclacene bond lengths, except for the terminal rings of polyacenes. Electronic effects discussed below, rather than strain factors proposed earlier,³ cause the unusual geometries of these molecules.

These generalizations about the geometries of the cyclacenes and polyacenes also apply to other mixed polyacenes. For example, calculations on linear polyacenes having unsaturated five-membered terminal rings, **4**,¹⁸ or heterocyclic terminal rings, **5**,^{19,20} predict bond length trends such as those found for polyacenes. The apparent reduction in delocalization across the benzene rings in the cyclacenes—to lengths expected for sp^2 – sp^2 single bonds—is not due to the strain of the cyclic system, but is an inherent electronic feature of system having consecutive linearly fused benzene rings, regardless of the end groups.



The electronic properties of cyclacenes reflect their bis-trannulene nature. The band gaps and singlet–triplet gaps of these compounds, and those of corresponding polyenes, or “polyacetylenes,” are summarized in Table 1 and Figure 3. The value of n refers to the number of

double bonds in the linear polyene, or number of benzene rings in the cyclacenes and polyacenes. When $n = \text{even}$, the singlet–triplet gap in cyclacenes is nearly constant around zero, and the value increases slightly as n increases; here, each trannulene is a $4n\pi$ electron anti-aromatic, but this anti-aromaticity is alleviated as the ring size increases.³ The opposite trend is observed for the $n = \text{odd}$ series; here, the cyclacene consists of two aromatic trannulenes,⁴ and the singlet–triplet gap gradually decreases, until $n = 9$, which has nearly degenerate singlet and triplet states. In the linear polyacenes there is no dichotomy between odd and even numbers of benzene rings as in the case of the cyclacene. The singlet–triplet gap gradually decreases as n increases. A triplet ground state is predicted at $n = 9$, identical to the prediction for $n = \text{odd}$ cyclacenes.

All larger systems also have triplet ground states. This means that the insulator, benzene, will gradually become a semiconductor as benzenes are fused and the band gap narrows, and eventually the band gaps disappears and the system becomes in effect two parallel doped polyacetylenes. Interesting and useful electrical and magnetic properties may result from such electronic structures. Indeed, relatively small polyacenes such as crystalline pentacene have proven their worth in several types of electronic devices.⁶

The singlet–triplet and singlet–singlet band gaps of polyacenes are uniformly smaller than those of the corresponding polyacetylene. This is related not only to the presence of two parallel polyacetylenes in a polyacene, but to the fact that polyacetylenes have alternating double and single bonds, while each strand of the polyacene has no bond alteration.

Both the polyacene and cyclacene series consist of two fully delocalized polyacetylenic (or trannulene) ribbons. However, both series violate standard features of polyacetylene chemistry in that there is no bond alternation along the ribbons, and both series are predicted to attain a zero singlet–triplet gap and consist of a triplet ground state for nine or more fused benzenes. By contrast, in polyacetylenes, the Peierls distortion leads to bond alternation, a singlet ground state, and a band gap of about 1.4 eV even for a hypothetical infinite polyacetylene. The triplet ground state is achieved for the 18 carbon trannulene unit in cyclanonacene. For comparison, octadecanonacene, the linear 18 carbon polyacetylene, is predicted to have a 0.76 eV singlet–triplet gap with the same computational method.

Nearly two decades ago, Kivelson and Chapman predicted that polyacenes might have conducting properties.⁸ Kertesz and Hoffmann described polyacenes and aromatics with additional layers of benzene rings.⁷ The limit of infinite polyacene in two dimensions is graphite, which has all bond lengths equal to 1.40 Å. Kertesz and Hoffmann described how the nonbonding orbitals of what we now call a trannulene interact strongly in a 1,2-fashion and weakly in a 1,4-fashion. They conclude that each “trannulene” will have bond alternation until three or more ribbons are united.⁷

In contrast, the B3LYP calculations reported here predict that large polyacenes consisting of only two polyacetylene ribbons have nonalternating structures joined by long bonds between ribbons. In polyacetylene itself, the Peierls instability of the hypothetical nonalternating polyacetylene causes the system to distort by bond alternation.²¹ This stabilizes the degenerate system,

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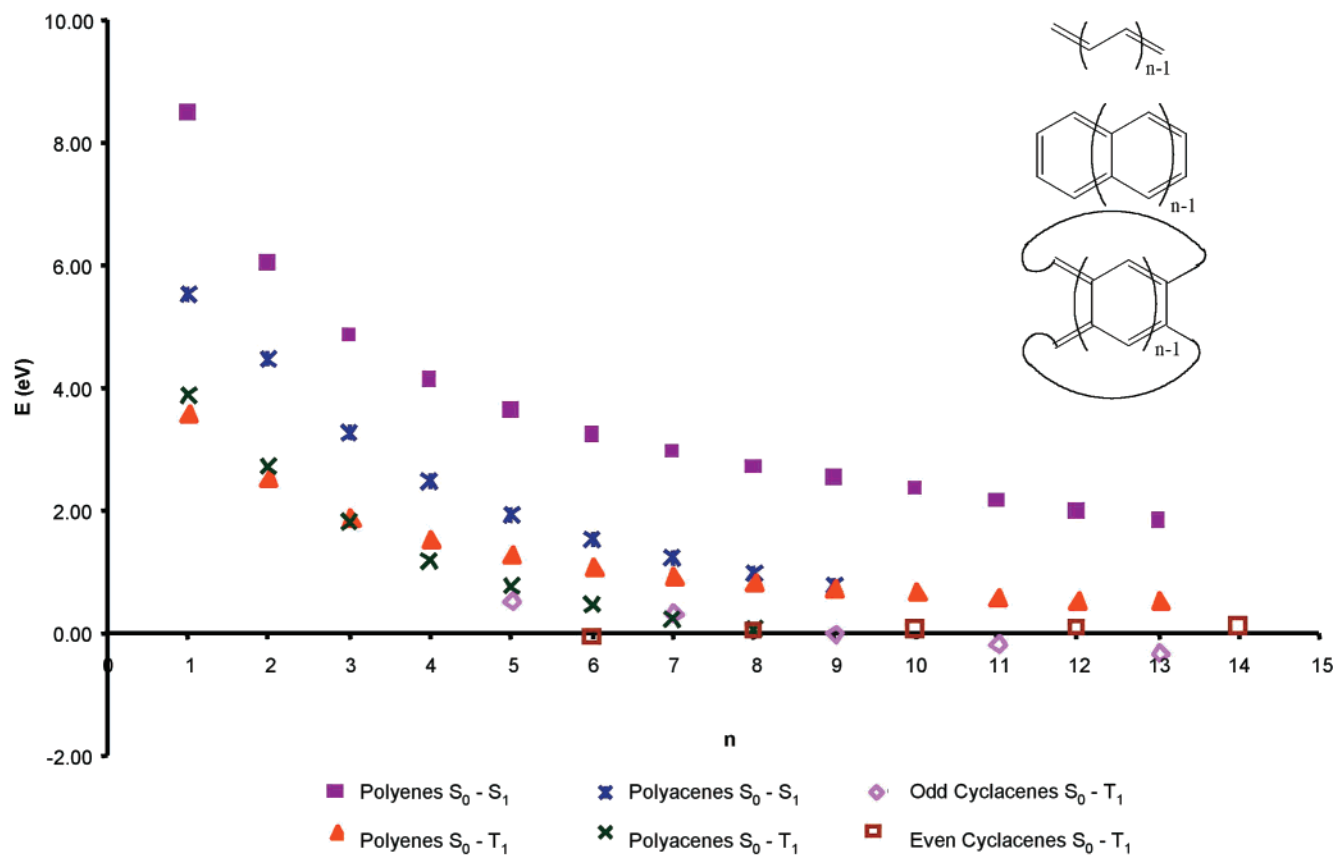


Figure 3. Computed S_0 - T_1 energy gaps for polyenes, polyacenes, and cyclacenes.³ Computed S_0 - S_1 energy gaps are also given for polyenes and polyacenes.

as can be rationalized by the simple model described below. We first describe the distortion of polyacetylene, and then show how systems such as polyacetylene can undergo stabilizing geometrical changes without causing bond-alternation of each polyacetylene ribbon. A similar model was used earlier to rationalize the unusual geometry of *s*-indacene ($4, n = 1$).²²

An infinite polyacetylene with all equal bond lengths has two degenerate singly occupied nonbonding MOs, which can be represented either as set A or as set B shown in Figure 4. A system of two degenerate orbitals can be represented as any linear combination of those orbitals. Sets A and B are the most usual representations, with nodes through every other bond, or nodes through every other atom, respectively. Using set A, it is easy to see that bond alternation can lead to stabilization. The shortening of every other bond and lengthening of those between, splits the degeneracy of the two singly occupied orbitals of set A by stabilizing one orbital of set A, and destabilizing the other orbital. The two odd electrons can then pair up and enter the more stable orbital.²¹

A similar MO model reveals the mechanism whereby polyacenes and cyclacenes have structures that maintain two nonalternating polyacetylene ribbons.⁵ A related model was presented by Kertesz and Hoffmann some time ago.⁷ Figure 5 shows schematically the four degenerate nonbonding orbitals of two noninteracting nonalternating polyacetylene ribbons. The orbitals are labeled

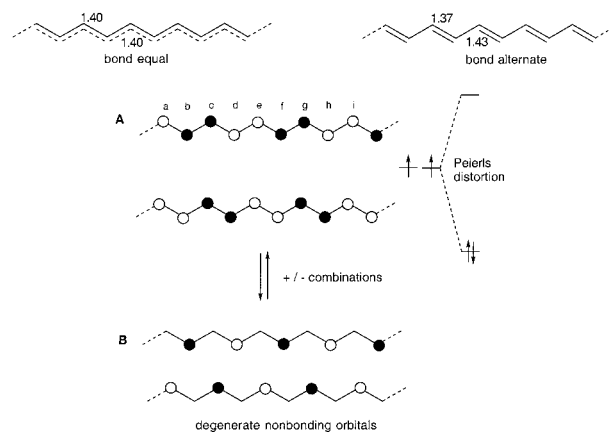


Figure 4. NBMOs of an all-1.40 Å polyene and Peierls distortion that splits degeneracies.

φ_a and φ_b for the bottom ribbon and φ_a' and φ_b' for the top ribbon. For example, these would represent two polyacetylenes very far apart. These orbitals are analogous to set A in Figure 4. If the two polyacetylenes are brought together to interact, as in polyacenes or cyclacenes, the MOs φ_a and φ_a' are of the same symmetry and can mix to form a bonding combination, $1/\sqrt{2}(\varphi_a + \varphi_a')$, which is stabilized and can accommodate and stabilize two electrons. The antibonding combination, $1/\sqrt{2}(\varphi_a - \varphi_a')$, gives a destabilized unoccupied MO. φ_b and φ_b' can also mix, but these overlap less well in the 1,4-sense, and the mixing is small. Consequently, combinations $1/\sqrt{2}(\varphi_b \pm \varphi_b')$ are nearly degenerate. For an infinite or very large polyacene or cyclacene, each of these are singly occupied

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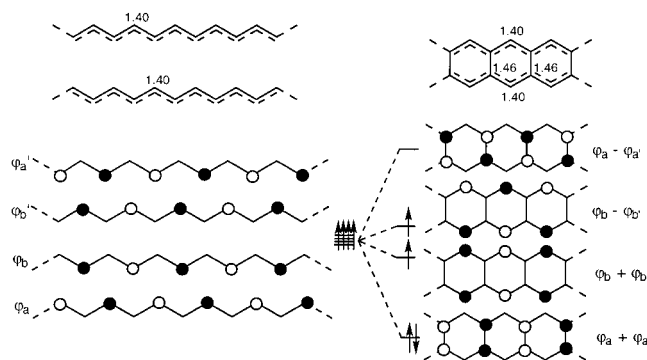


Figure 5. NBMOs of top and bottom all-1.40 Å ribbons of polyacenes and cross-ring Peierls' distortions that splits one degeneracy but leaves a near-degenerate pair of NBMOs.

because the electron-repulsion of the two electrons in one orbital exceeds the orbital energy gap. A triplet ground-state results.

For small polyacenes such as benzene and up to octacene, a singlet ground state results, because even this 1,4 interaction is relatively large. In benzene, the coefficients of the NBMOs involved in the 1,4 interaction are both $1/\sqrt{2}$, the interaction is large, and the triplet is much above the singlet ground state. However, by nonacene, these coefficients are $1/\sqrt{18}$, resulting in a very small 1,4 interaction and a triplet ground state.

Previous authors had considered that the normal type of Peierls distortion of the two polyacetylene ribbons would occur to give structures **3b** or **3c**.^{7–10} However, we do not find these as energy minima, but only a vibrationally excited polyacenes.

The predicted structures of polyacene and cyclacenes according to B3LYP have long bonds connecting the two ribbons; alternating bonds do not occur in the two parallel ribbons. Figure 2 summarizes these generalizations. This

is the same type of model we developed earlier to rationalize the anomalous geometry of the formally anti-aromatic twelve π electron *s*-indacene.²² It is fruitful to think of the polyacenes as in Figure 2 or represented in **3a**, essentially as nonalternating polyacetylenes joined by single bonds and very weak π interactions. The long bond connecting the two parallel ribbons in polyacenes becomes shorter in systems with more parallel ribbons, culminating in graphite, where all bond lengths are equal.

Conclusion

B3LYP calculations provide predicted structures and electronic properties of polyacenes. Of particular note are the differences between these aromatic structures—that nevertheless imbed two low- or zero-band gap polyacetylene ribbons. The low band-gaps and bond equalization of linear polyacenes endow them with properties suitable for electronic device application⁶ and potential for non-linear optical properties in suitably modified forms.²³

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research and to the Office of Academic Computing at UCLA and the National Center for Supercomputing Applications, Urbana-Champaign, for computer resources.

Supporting Information Available: Cartesian coordinates and energies from B3LYP/6-31G* calculations for singlet and triplet states of polyenes, ethylene through octadodecatetradecene, and polyacenes, benzene through nonacene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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