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Research Article

SYNTHESIS, CRYSTAL STRUCTURE, HIRSHFELD SURFACE, ENERGY FRAMEWORK ANALYSIS OF A TETRAPHENYL BENZENE

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ABSTRACT

Phenyl benzene derivatives are important from medicinal point of view because of their widespread biological significance. In the present work the title compound, having molecular formula, C_{30} H_{22} has been synthesized and characterized by XRD, Hirshfeld surface and energy framework analysis. Single crystal x-ray diffraction analysis shows that the title compound crystallizes in orthorhombic system with space group Pbcn. Tetra phenyl benzene exhibits a symmetrical structure. The molecule exhibits C-H…π interactions forming corrugated sheets. The bright red spot shows the C-H…π interactions in the title compound which confirms the XRD results. The red and blue triangle on the shape index and the large flat region on the curvature refer to the C-H…π interactions.

Keywords: Phenyl derivative, C-H…π interactions, Hirshfeld surface analysis, Energy framework.

1. INTRODUCTION

The benzene derivatives with multiple contiguous phenyl substituents have much more complex, non-planar topologies than planar molecules. These non-planar topologies competently limit conjugation and inhibit extensive aromatic π-π and C-H…π interactions. The benzene derivatives with several adjacent phenyl substituents have many possible applications in various areas of science. It finds applications in optoelectric devices, template materials for supramolecular assembly, and the synthesis of equivalents of graphene [1-10]. These compounds show properties like highest occupied molecular orbital, lowest-unoccupied molecular orbital gaps, lower degrees of self-association, less efficient packing, and higher solubility than planar analogues with similarly high thermal stability [11-12].

These benzene derivatives modify the plane conjugate chromophore in optical applications [6-10]. The introduction of the dendritic benzene cause quenching. These potential effects allow thin films to be processed from solution as long-lived amorphous phases with high values of T_g. Literature survey tells that benzene-cored luminophors exhibited aggregation-induced emission properties and the mechanism could be attributed to the restriction of intramolecular rotations [13-15]. Many derivatives of tetraphenyl benzene are anti-arrhythmic agents [16-18]. The tetraphenyl ring system shows many conformations, like twin-chair, chair-boat, boat-chair and twin-boat conformations [19-22]. Intermolecular interactions are due to the tendency of molecules to pack as closely as possible upon crystallization. Predicting the crystal structures of such interactions are difficult due to the complex nature. Symmetrically shaped molecules are anticipated to provide under-standings into the nature of intra and inter-molecular interactions. Tetraphenyl benzene systems are one among them of pharmacological importance and are possibly interesting as anticholinergic compounds [23]. Now-a-days tetraphenyl and its derivatives, are of intense interest, because of their structure and electronic properties of which they are used as hole-injecting and transporting layer materials in a wide range of electrooptic devices [24-28]. Tetra-phenyls are used as dyes, thermal printing materials or coolants, in technological industries.

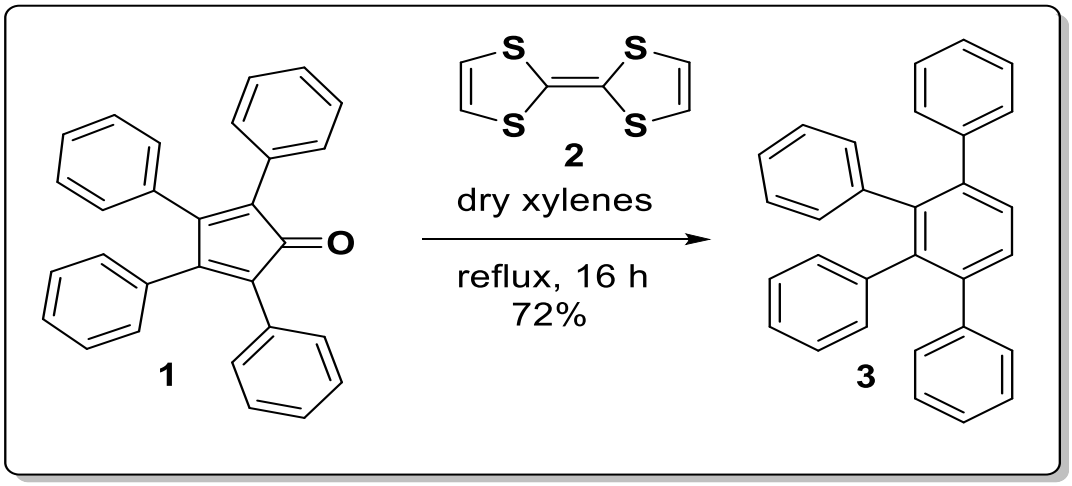
In this present work, the structure of the title compound was determined by X-ray crystallography. The contribution percentage of intermolecular contacts in the crystal structure is determined with the fingerprint plots analyzed by the Hirshfeld surface technique. To analyze the nature of interactions present

in the molecule, Hirshfeld surface and 2D fingerprint plot studies were performed. The intermolecular interaction energies were also calculated and their distribution over the crystal structure were visualized graphically using energy frameworks.

2. EXPERIMENTAL

2.1. Synthesis of title compound

To a solution of tetraphenylcyclopentadienone1(0.31 g, 0.80 mmol) in dry xylenes (15 mL), tetrathiafulvalene (TTF) 2 (0.15 g, 0.73 mmol) was added and refluxed for 16 h. Removal of xylenes in vacuo followed by column chromatographic purification (silica gel, 100% hexane) afforded 1,2,3,4-tetraphenylbenzene 3 (0.295 g, 72%) as an orange solid; mp 182-184°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.41 (s, 2H, ArH), 7.04 (s, 10H, ArH), 6.83-6.81 (m, 6H, ArH), 6.73-6.70 (m, 4H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.9, 140.9, 140.4, 139.9, 131.6, 129.9, 129.5, 127.6, 126.9, 126.3, 125.7 ppm; DEPT 135-NMR (75 MHz, $CDCl_3$): δ 131.6, 129.9, 129.5, 127.6, 127.0, 126.3, 125.7 ppm.



Scheme 1: Schematic diagram of title compound

2.2. Characterization techniques

A Bruker AXS (Kappa Apex II) X-ray diffractometer was used for single crystal XRD studies at 296K with graphite monochromatic MoK_α radiation of wavelength (λ)=0.71073 Å. Hirshfeld surface analysis, energy framework and fingerprint plots were generated by Crystal Explorer (Version 17.5) program [29].

3. RESULTS AND DISCUSSION

3.1. X-ray crystallography

Data were corrected for Lorentz-polarization and absorption factors. The structure was solved by direct methods using SHELXT-2014/4 [30] and refined using SHELXL2014/7 [31], by full matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and H atoms were localized from the difference electron-density maps and refined as riding atoms with C-H = 0.93 or 0.97 Å with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for other H atoms. The geometrical calculations were carried out using the program PLATON [32]. The molecular and packing diagrams were generated using the software MERCURY [33].

The molecular structure of the title compound is shown in Fig. 1. The crystal packing of title compound showing the C-H…π interactions is shown in Fig. 2. Tetraphenyl benzene exhibts a symmetrical structure. It has four benzene rings attached to the central benzene ring. The dihedral angle between the central benzene ring (C7-C8-C15-C7a-C8a-C15a) and the atoms (C9-C14), (C1-C6) are 68.76 (11)º and 50.24(11)° respectively. The torsion angles for C4-C5-C6-C7 and C13-C14-C9-C8 are 174.32° and 176.22°. The molecule exhibits C-H…π interactions forming corrugated sheets (fig.2). The crystal data and structure refinement details are given in Table 1. The selected bond lengths, bond angles, and torsion angles are listed in Tables 2, 3, and 4 respectively.

Table 1: Crystal data and structure refinement for the title compound

Empirical formula	$C_{30}H_{22}$	
Formula weight	382.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 23.549(3) Å	α= 90°
	b = 9.0441(11) Å	β= 90°
	c = 10.0262(11) Å	γ = 90°
Volume	2135.3(4) $Å^3$	
Z	4	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	808	
Crystal size	0.250 x 0.200 x 0.200 mm^3	
Theta range for data collection	2.412 to 24.995°.	
Index ranges	-28<=h<=27, -10<=k<=10, -11<=l<=11	
Reflections collected	24484	
Independent reflections	1880 [R(int) = 0.0626]	
Completeness to theta = 24.995°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6815	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1880 / 0 / 137	
Goodness-of-fit on F^2	1.121	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1199	
R indices (all data)	R1 = 0.0972, wR2 = 0.1775	
Extinction coefficient	0.017(3)	
Largest diff. peak and hole	0.156 and -0.140 $e.Å^{-3}$	

Table 2: Bond lengths [Å] for title compound

C(1)-C(2)	1.380(4)
C(1)-C(6)	1.386(3)
C(2)-C(3)	1.366(4)
C(3)-C(4)	1.368(4)
C(4)-C(5)	1.378(3)
C(5)-C(6)	1.388(3)
C(6)-C(7)	1.490(3)
C(7)-C(15)	1.384(3)
C(7)-C(8)	1.407(3)
C(8)-C(8)#1	1.407(4)
C(8)-C(9)	1.492(3)
C(9)-C(14)	1.382(3)
C(9)-C(10)	1.383(3)
C(10)-C(11)	1.385(4)
C(11)-C(12)	1.376(4)
C(12)-C(13)	1.357(4)
C(13)-C(14)	1.374(3)
C(15)-C(15)#1	1.366(4)

Table 3: Bond Angles [Å] for title compound

C(2)-C(1)-C(6)	121.2(3)
C(2)-C(1)-H(1)	119.4
C(3)-C(2)-C(1)	120.1(3)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(2)-C(3)-C(4)	119.8(3)
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	120.4(3)
C(3)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	121.0(3)
C(4)-C(5)-H(5)	119.5
C(5)-C(6)-C(7)	122.6(2)
C(15)-C(7)-C(8)	118.2(2)
C(15)-C(7)-C(6)	117.6(2)
C(7)-C(8)-C(8)#1	120.12(12)
C(8)#1-C(8)-C(9)	119.36(11)
C(14)-C(9)-C(10)	118.1(2)
C(9)-C(10)-C(11)	120.1(2)
C(9)-C(10)-H(10)	119.9
C(12)-C(11)-C(10)	120.5(2)
C(12)-C(11)-H(11)	119.8
C(13)-C(12)-C(11)	119.6(3)
C(13)-C(12)-H(12)	120.2
C(12)-C(13)-C(14)	120.3(3)
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(9)	121.3(2)
C(13)-C(14)-H(14)	119.3
C(15)#1-C(15)-C(7)	121.67(13)
C(7)-C(15)-H(15)	119.2

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

Table 4: Torsion angles [°] for title compound

C(2)-C(1)-C(6)-C(7)	174.3(2)
C(4)-C(5)-C(6)-C(7)	-174.3(2)
C(5)-C(6)-C(7)-C(15)	127.7(2)
C(6)-C(7)-C(8)-C(8)#1	-178.4(2)
C(15)-C(7)-C(8)-C(9)	-174.98(18)
C(8)-C(9)-C(10)-C(11)	176.8(2)
C(8)-C(9)-C(14)-C(13)	-176.2(2)
C(6)-C(7)-C(15)-C(15)#1	-178.6(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

3.2. Hirshfeld Surface Analysis

The data obtained from single crystal XRD analysis were used to generate the Hirshfeld surface [34-35]. Crystal Explorer version 17.5 software was used to analyze the intermolecular contacts by generating Hirshfeld surface using the CIF as input file. 2D fingerprint plots were used to see the graphical visualization of the intermolecular contacts. The factor d_{norm} has been used to analyse the intermolecular contacts with the combination of three colours red, blue and white. It comprises of two elements, d_e, and d_i which denotes the distance of any surface point nearest to the interior atoms and the distance of the surface point nearest to the exterior atoms respectively, and also with the van der Waals (vdW) radii of the atom [36-38]. The red colour circular spots indicate closer hydrogen bonding contacts with negative d_{norm} value. The blue colour indicates longer contacts with positive d_{norm} value, and the white colour indicates the intermolecular distances close to Van der Waals radii with d_{norm} value equal to zero [39]. The shape index indicates the shape of the electron density surface around the molecular interactions.

Fig. 3 shows the Hirshfeld surface mapped over d_{norm}, electrostatic potential, shape index, curvature, and fragment patches for the title compound. The bright red spot shows the C-H…π interactions in the title compound which confirms the XRD results. The red and blue triangle on the shape index and the large flat region on the curvature refer to the C-H…π interactions. The fragment patches shows the co-ordination environment of the molecule

The complete two-dimensional fingerprint plot, is shown in Fig. 4. The H…H interactions has the maximum contribution with overall Hirshfeld surface of 66.2% in the title compound. The C…H interactions can be seen as sharp spikes in fingerprint plot showing a contribution of 33.8% of the Hirshfeld surfaces in title compound.

3.3. Energy Framework analysis

The four components electrostatic, polarization, dispersion and exchange repulsion expresses the interaction energy between the molecules. These energies were obtained using monomer wavefunctions calculated at the HF/3-21G. The total interaction energy, which is the sum of scaled components, was calculated for a 3.8 Å radius cluster of molecules around the selected molecule as shown in Fig. 5. The interaction energies calculated by the energy model discloses that the interactions in crystal have a important contribution from dispersion components of compound (Table 2). The absence of the hydrogen bond interaction energies are represented graphically using energy frameworks and the supramolecular architecture of the crystal structures are shown in Fig 5b-5d.

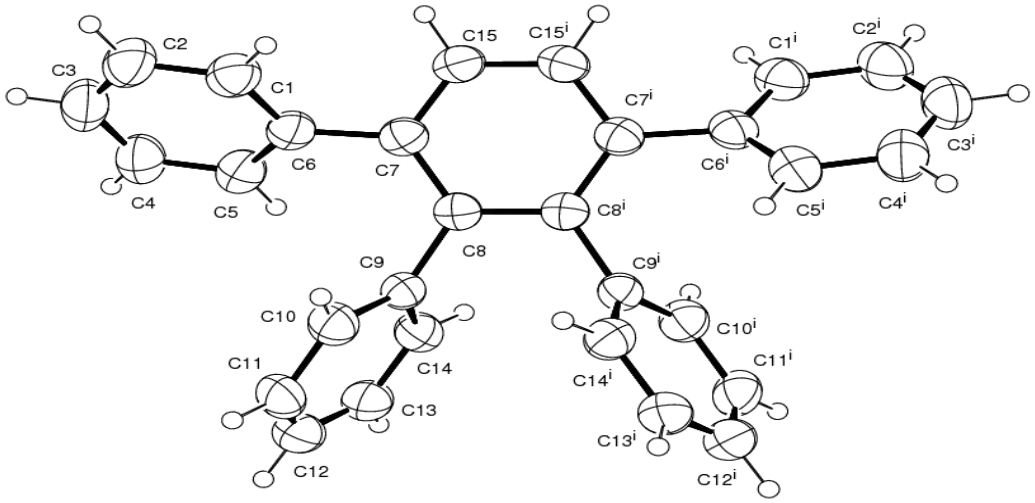


Fig. 1: The molecular structure of the title compound with 40% probability displacement ellipsoids for non-H atoms

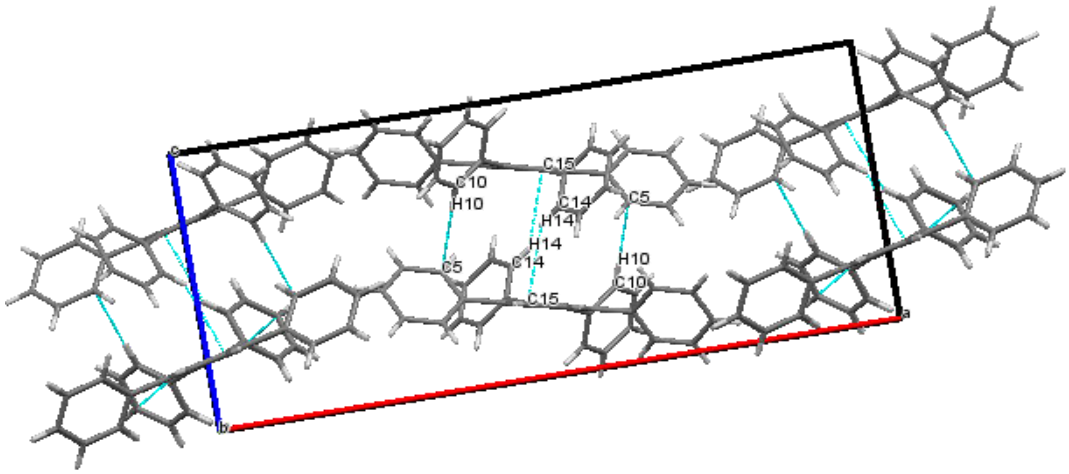


Fig. 2: The crystal packing of title compound showing the C-H…π interactions

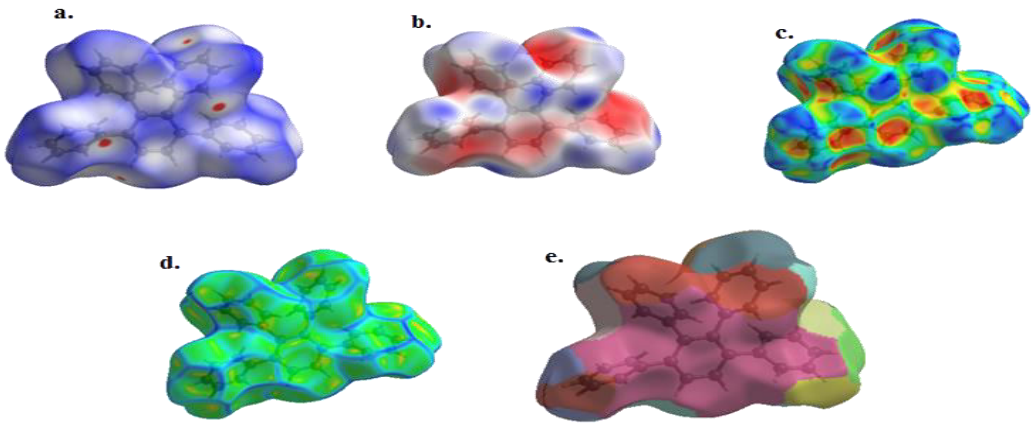


Fig. 3: View of the Hirshfeld surface of title compound mapped over a) d_{norm} and b) electrostatic potential c) shape index d) curvature e) fragment patches

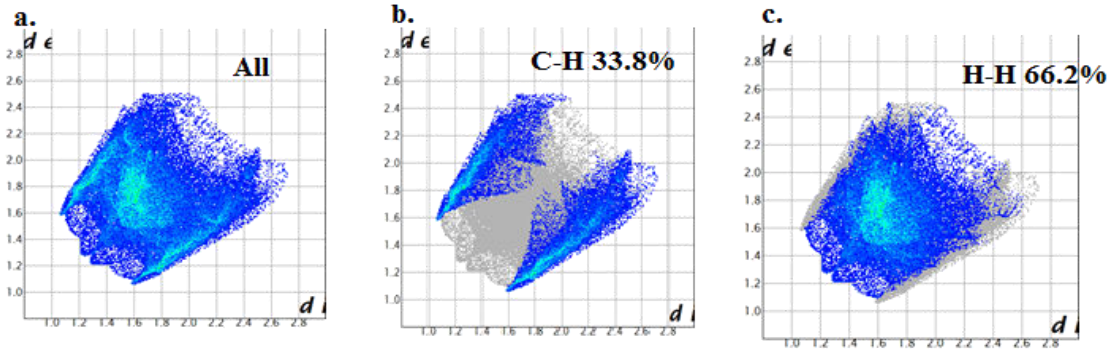


Fig. 4: The two-dimensional fingerprint plots for (*a*) all interactions, (*b*) C…H, (*c*) H…H

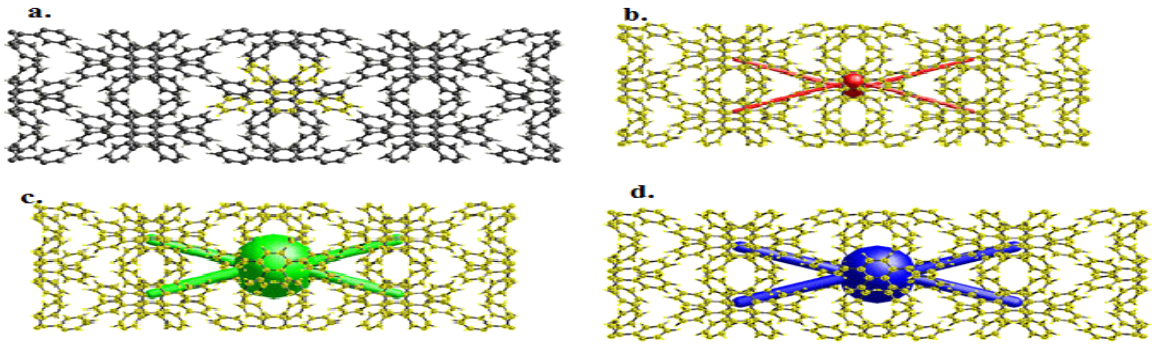


Fig. 5: (a) Interactions between the selected reference molecule (highlighted in yellow) and the molecules present in a 3.8 A ° cluster around it, (b) Coulomb energy framework, (c) dispersion energy framework and (d) total energy framework

Table 5: Scale factors for benchmarked energy models

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF … HF/3-21G electron densities	1.019	0.651	0.901	0.811

Table 6: Interaction energies (kJ mol^{-1}) for title compound between a reference molecule and its neighbours

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-x, -y, -z	5.17	HF/3-21G	-21.9	-4.3	-86.1	44.8	-66.4
2	x+1/2, y+1/2, -z+1/2	12.61	HF/3-21G	-5.2	-1.1	-16.2	6.9	-15.0
2	-x+1/2, -y+1/2, z+1/2	13.21	HF/3-21G	0.4	-0.0	-2.6	0.0	-2.0
	Total			-26.7	-5.4	-104.9	51.7	-83.4

4. CONCLUSION

The title compound was synthesized and the structure was confirmed using x-ray diffraction method. In the crystal, molecules are linked by C-H… π interactions. The Hirshfeld surface analysis confirms the XRD data of intermolecular interactions as bright red spots. The red and blue triangle on the shape index and the large flat region on the curvature refer to the C-H…π nteractions. The absence of the hydrogen bond interaction energies are represented graphically using energy frameworks.

5. SUPPLEMENTARY DATA

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers: 1867917.Copies of this informationmay be obtained free of the charge from the Director, CCDC, 12 Union Road,Cambridge, CB2 1EZ, UK (Fax: +44-

1223-336033; E-mail: deposit@ ccdc.cam.ac.uk orhttp://www.ccd.cam.ac.uk).

6. ACKNOWLEDGEMENTS

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Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this article.

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