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Polymorphism of Crystalline Inclusion Complexes and Unsolvated Hosts. Part 8.⋆ Endocyclic Modification of the Cyclotriveratrylene Host-Guest Complex with Acetone

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Abstract. Crystallization of cyclotriveratrylene (CTV) from solutions in acetone at 40°C gave a new 4 : 1 host-guest complex instead of the conventional 2 : 1 clathrate (β-phase) whose X-ray crystal structure was determined. Data for $2(C_{27}H_{30}O_6) \cdot 0.5(CO(CH_3)_2)$: monoclinic, $P2_1/c$, a = 18.942(4), b = 24.697(5), c = 10.508(2) Å, β = 91.10(2)°, V = 4915(2) Å^3, Z = 8, D_x = 1.257 g/cm^3, T = 293 K, R = 0.077 (for 2694 reflections). One of the two crystallographically independent CTV molecules (molecule A) is stacked into columns characteristic of the CTV α- or β-phase complexes. Molecules B face each other enclathrating inside around the inversion center disordered acetone molecules giving rise to the molecular capsule. The acetone molecule is H-bonded simultaneously to both host molecules by C(H_2)–H · · · O type bonds forming centrosymmetric dimers. Dimers are incorporated together with two A molecules into centrosymmetric units also by C(H_2)–H · · · O type H-bonds. Packing of these units gives rise to the crystal structure of the clathrate.

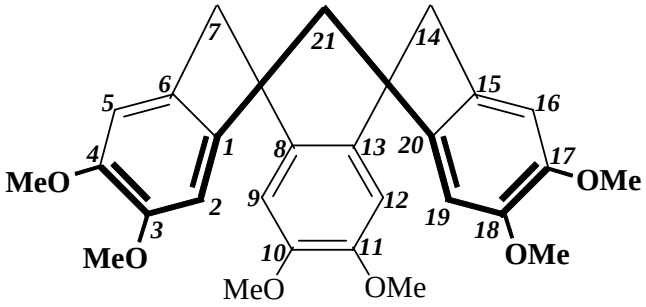
Key words: cyclotriveratrylene, host-guest complex, X-ray structure.

Supplementary data relevant to this article have been deposited with the British Library Publication.

1. Introduction

CTV (**I**), first investigated in 1915 by Robinson [1], has attracted attention in view of its ability to form crystalline inclusion complexes with small molecules. This property of CTV was mentioned for the first time by Bhagwat *et al.* [2] in 1931 and investigated comprehensively by Gaglioti *et al.* [3, 4] 25 years later. The first CTV crystal structure was solved by Cerrini *et al.* [5] in the example of its benzene-water complex. In 1990 Atwood and Zhang [6] determined the crystal structure of unsolvated CTV. A detailed study of CTV clathrates was carried out by the same group in 1994. They have established X-ray crystal structures of the CTV clathrates

⋆ Part 7 is reference 14.



I

with water, toluene-water and chloroform relating to α-phase complexes and with acetone and dimethoxyethane (β-phase complexes) [7].

Beginning in the early 1980s an interest in macrocyclic host compounds was shifted towards the use of their rigid structure for entrapping neutral or charged molecular species [8]. In CTV clathrates guest molecules are usually located out of the host cavity [5, 7, 9], i.e., it turns out that all CTV crystalline supramolecular associates are exocyclic complexes [10]. Intracavity type complexes have been recently obtained for unusual guest molecules such as neutral fullerenes [11], carboranes [12] and charged organometallic sandwich complexes [13]. Therefore a preparation of CTV intramolecular complexes with ordinary solvent molecules is of great scientific and practical interest and important for CTV host-guest chemistry. As we are dealing with polymorphism of crystalline host-guest complexes of versatile hosts and have succeeded in the preparation of some unusual modifications of definite host-guest pairs [14–17] and as this problem is found to be important we have investigated crystallization of CTV from its solution in acetone hoping to find an endocyclic modification of the complex. We have obtained a new modification of the CTV-acetone complex of the endocyclic type rather than its conventional 2 : 1 exocyclic complex. The preliminary results obtained were already reported [18]. The present paper is devoted to the detailed discussion of the X-ray crystal structure of this complex.

2. Experimental

Single crystals of the CTV-acetone complex were obtained by evaporation of the solvent from CTV solutions in acetone placed into a thermostat at 40 °C. A prism shaped crystal with dimensions 0.06 × 0.10 × 0.4 mm was used for all measurements on a Syntex-$P2_1$ diffractometer. Lattice parameters were determined by a least-squares fit of the setting angles of 15 reflections with 2θ in the range 20–25° (Table I).

Reflection intensities were measured with graphite monochromatized CuK_α-radiation up to $2\theta_{max}$ = 118°. No significant intensity variation was observed for standard reflections monitored after each group of 100 reflections. Integrated in-

Table I. Crystal data and structure refinement for CTV · acetone (4 : 1) complex

Empirical formula	$2(C_{27}H_{30}O_6) \cdot 0.5(CO(CH_3)_2)$
Formula weight	930.06
Temperature/K	293(2)
Wavelength/Å	1.54178
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions/Å/°	a = 18.942(4) α = 90
	b = 24.697(5) β = 91.10(3)
	c = 10.508(2) γ = 90
Volume/Å^3	4915(2)
Z	4
Density (calculated)/g · cm^{-3}	1.257
Absorption coefficient/mm^{-1}	0.719
F(000)	1984
Crystal size/mm	0.06 × 0.10 × 0.4
Theta range for data collection/°	2.33 to 59.35
Index ranges	$0 \Leftarrow h \Leftarrow 21$, $-27 \Leftarrow k \Leftarrow 0$, $-11 \Leftarrow l \Leftarrow 11$
Reflections collected	7145
Independent reflections	7112 [R(int) = 0.1534]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7112/0/622
Reflections with F>4 σ(F)	2694
Goodness-of-fit on F^2	0.927
Final R indices [F>4 σ(F)]	R1 = 0.0775, wR2 = 0.1217
R indices (all data)	R1 = 0.2170, wR2 = 0.1540
Extinction coefficient	0.000502
Largest diff. peak and hole/e · Å^{-3}	0.153 and −0.221

tensities were collected by the $\theta/2\theta$-method. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using the program SHELXS-86 [19]. Practically all non-hydrogen atoms of the two crystallographically independent host molecules were located from the best E-map. Subsequent difference Fourier syntheses revealed the positions of the remaining non-H atoms of the host and guest. The guest molecule is required to be disordered in the two positions since it is placed on the inversion center.

The structure has been refined by the full-matrix least-squares method first with isotropic and then with anisotropic temperature factors using the program SHELXL-93 [20]. The positions of H-atoms were found from difference Fourier maps except for the hydrogen atoms of the solvent molecule, the $C(26)H_3$-

group and the C(12) atom. Coordinates of these H-atoms were calculated on the basis of stereochemical rules. The refinement of the structure converged with final R1=0.077 and wR2=0.122. Final atomic coordinates are given in the Table II.

3. Results and Discussion

The unit cell parameters of the CTV-acetone 4 : 1 complex are not related to any known phases and is a representative of a new type. The complex is crystallized with two CTV molecules, *A* and *B*, in the asymmetric part of the unit cell and according to the results of the X-ray investigation it indeed belongs to a novel group of CTV clathrates.

3.1. MOLECULAR STRUCTURE

The nine-membered ring of these molecules having a trigonal symmetry in the free state is in a stable crown conformation while the whole molecule has a cone form. A crown conformation may be characterized by the angle between the benzene rings and the plane of the three methylene carbon atoms of the crown and by the distances between benzene ring centers. Dihedral angles between the plane of the C(7), C(14) and C(21) atoms and C(1)–C(6), C(8)–C(13) and C(15)–C(20) benzene rings are equal to 38.0, 47.9 and 46.1° in molecule *A* while these angles for molecule *B* are 44.1, 42.2 and 42.8°, respectively (Figure 1). The distances between benzene rings are equal to 4.60, 4.79 and 4.82 Å for molecule *A* and 4.77, 4.76 and 4.71 Å for molecule *B*. The aromatic hydrogen atoms of the two neighboring benzene rings are directed towards each other and are virtually at normal contact distances (2.38–2.46 Å) while pseudo-axial hydrogens of the methylene bridges are at steric repulsion distances (2.16-2.23 Å for molecule *A* and 2.03–2.10 Å for molecule *B*). The above values defining the conformation of the two independent CTV molecules show that a slightly greater deviation from trigonal symmetry is observed for molecule *A* by comparison with molecule *B*. These values are, however, in good agreement with ones found in other CTV crystals [5–7] since the conformation of the CTV molecule is fairly rigid.

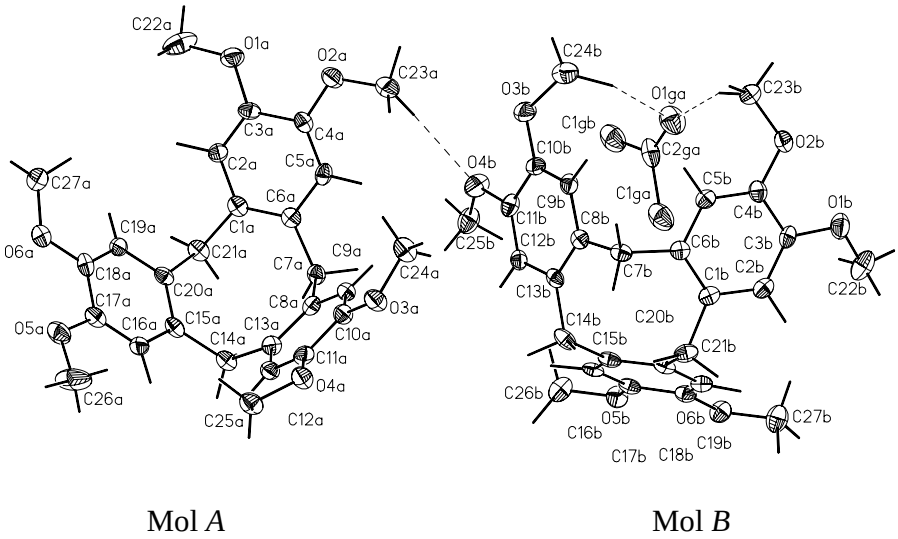
Nevertheless, CTV molecules may not have identical conformations in the different crystal forms because of the conformational lability of the methoxy groups. Methyl groups may be coplanar with atoms of the respective aromatic ring and may be oriented inside or outside of the CTV molecule cone [5–7, 9]. A coplanarity of the benzene ring atoms and deviations of the methoxy group non-hydrogen (non-H) atoms from the respective planes are shown in Table III. The atoms of only one aromatic ring of each independent host molecule are nearly coplanar with the respective methoxy group non-H atoms; those rings are C(1A)–C(6A) and C(15B)–C(20B). The methyl groups of the other two rings of both CTV molecules deviate from the appropriate ring plane inward molecules to different extents but not more than about 0.60 Å. Groups $C(24B)H_3$, $C(25B)H_3$ and $C(23B)H_3$ deviate at the

Table II. Non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for CTV · acetone (4 : 1). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
C(1A)	5222(3)	3615(2)	733(5)	49(1)
C(2A)	4899(3)	3933(2)	1642(5)	52(1)
C(3A)	5279(3)	4217(2)	2541(5)	54(2)
C(4A)	6019(3)	4197(2)	2517(5)	52(1)
C(5A)	6338(2)	3900(2)	1601(5)	52(1)
C(6A)	5952(3)	3591(2)	711(5)	50(1)
C(7A)	6353(2)	3253(2)	−229(4)	52(1)
C(8A)	6557(3)	2698(2)	294(5)	49(1)
C(9A)	7114(3)	2659(2)	1165(5)	52(2)
C(10A)	7310(3)	2189(2)	1768(5)	55(1)
C(11A)	6942(3)	1718(2)	1428(5)	54(1)
C(12A)	6400(3)	1748(2)	542(5)	53(1)
C(13A)	6181(3)	2234(2)	−18(4)	50(1)
C(14A)	5512(3)	2212(2)	−812(4)	52(1)
C(15A)	4866(3)	2249(2)	14(5)	54(2)
C(16A)	4626(3)	1770(2)	584(5)	56(2)
C(17A)	4105(3)	1761(2)	1429(6)	59(2)
C(18A)	3805(3)	2252(3)	1826(6)	61(2)
C(19A)	4012(3)	2721(2)	1241(5)	52(1)
C(20A)	4551(3)	2737(2)	366(5)	47(1)
C(21A)	4752(3)	3288(2)	−175(4)	53(1)
C(22A)	4252(4)	4613(3)	3426(5)	107(2)
C(23A)	7105(3)	4501(2)	3423(6)	90(2)
C(24A)	8088(3)	2631(2)	3228(5)	73(2)
C(25A)	6646(3)	824(2)	2069(5)	69(2)
C(26A)	4227(4)	821(2)	1868(6)	133(3)
C(27A)	3080(3)	2723(2)	3289(5)	74(2)
O(1A)	5000(2)	4530(1)	3492(4)	74(1)
O(2A)	6362(2)	4501(1)	3445(3)	69(1)
O(3A)	7841(2)	2139(1)	2657(4)	70(1)
O(4A)	7158(2)	1250(1)	2035(3)	67(1)
O(5A)	3848(2)	1305(2)	2033(4)	78(1)
O(6A)	3290(2)	2225(2)	2723(4)	72(1)
C(1B)	1718(3)	1613(2)	6032(5)	47(1)
C(2B)	2288(3)	1291(2)	5646(5)	54(2)
C(3B)	2477(3)	820(2)	6274(5)	52(1)
C(4B)	2096(3)	667(2)	7333(5)	53(1)

Table II. Continued.

Atom	*x*	*y*	*z*	*U*(eq)
C(5B)	1552(3)	990(2)	7726(4)	48(1)
C(6B)	1347(3)	1461(2)	7094(5)	46(1)
C(7B)	715(3)	1767(2)	7591(4)	50(1)
C(8B)	19(3)	1530(2)	7093(4)	44(1)
C(9B)	−253(3)	1089(2)	7744(4)	54(2)
C(10B)	−848(3)	814(2)	7353(5)	55(2)
C(11B)	−1209(3)	997(2)	6272(5)	58(2)
C(12B)	−962(3)	1438(2)	5635(4)	50(1)
C(13B)	−334(3)	1705(2)	6007(4)	47(1)
C(14B)	−81(3)	2159(2)	5177(5)	57(2)
C(15B)	350(3)	1962(2)	4063(5)	49(1)
C(16B)	−33(3)	1779(2)	2997(5)	46(1)
C(17B)	294(3)	1573(2)	1954(5)	49(1)
C(18B)	1040(3)	1550(2)	1943(5)	49(1)
C(19B)	1417(3)	1735(2)	3003(5)	51(1)
C(20B)	1080(3)	1929(2)	4065(5)	49(1)
C(21B)	1532(3)	2098(2)	5213(5)	58(2)
C(22B)	3230(3)	503(3)	4665(6)	92(2)
C(23B)	1812(3)	−56(2)	8711(6)	85(2)
C(24B)	−649(3)	49(2)	8682(6)	85(2)
C(25B)	−2009(3)	735(2)	4612(6)	79(2)
C(26B)	−796(3)	1412(2)	884(5)	71(2)
C(27B)	2103(3)	1331(2)	888(5)	81(2)
O(1B)	3018(2)	479(2)	5944(4)	80(1)
O(2B)	2300(2)	193(2)	7917(3)	72(1)
O(3B)	−1127(2)	366(2)	7947(4)	82(1)
O(4B)	−1806(2)	708(2)	5906(4)	79(1)
O(5B)	−41(2)	1385(1)	876(3)	61(1)
O(6B)	1345(2)	1355(1)	872(3)	62(1)
C(1G)	−460(3)	−369(3)	5185(6)	98(2)
C(2G)	183(8)	−127(7)	5631(14)	80(4)
O(1G)	491(5)	−277(4)	6536(8)	103(3)



Mol *A* Mol *B*

Figure 1. Asymmetric part (2CTV : 0.5 acetone) of the unit cell in the CTV-acetone 4 : 1 complex and numbering scheme.

most extent towards acetone molecules located inside CTV molecules *B* in order to enable hydrogen bonding (H-bonding) between host and guest. Inward orientations of the other methyl groups are not caused by H-bonding and defined by the crystal packing forces.

3.2. CRYSTAL STRUCTURE

Gaglioti *et al.* [3, 4], on the basis of the data available at that time (IR and X-ray measurements), identified two types of CTV crystals relating only to the monoclinic system. For these types, named α- and β- phases, different values of the *b*-axis are characteristic (9.60–9.80 Å for the α-phase and 8.00–8.40 Å for the β-phase complexes). Crystallographic data of unsolvated CTV [6] and its host-guest complexes determined recently [7] did not violate this classification. The 9.60 Å length of the *b* axis for α-phase complexes is a consequence of the stacking of CTV molecules one in the cavity of the other forming columns along the *b* direction. In the case of the β-phase complexes columns are also formed but here the cavity of the CTV molecule is filled by the methoxy substituents of the closest molecule from the same column. In order to enable such disposition CTV molecules should be displaced in the lateral direction that results in the decreasing of the *b* translation. In spite of the absence in the CTV molecule of groups capable to be involved in the ordinary H-bonds, H-associates formed by $C(H_2)$—H···O type bonds are characteristic for its crystals [6, 7, 9].

In the CTV-acetone 4 : 1 complex molecules *A* are stacked into columns characteristic of the α-phase complexes. Two *B* molecules facing each other encapsulate

Table III. The deviations of the atoms (Å) from least-squares planes of the benzene rings in the structure of the CTV-acetone 4 : 1 complex

Atoms	Deviations	Atoms	Deviations	Atoms	Deviations
Molecule *A*					
C(1A)	−0.004	C(8A)	0.002	C(15A)	0.005
C(2A)	0.014	C(9A)	−0.019	C(16A)	0.004
C(3A)	−0.007	C(10A)	0.016	C(17A)	−0.022
C(4A)	−0.010	C(11A)	0.004	C(18A)	0.031
C(5A)	0.019	C(12A)	−0.021	C(19A)	−0.022
C(6A)	0.012	C(13A)	0.018	C(20A)	0.004
O(1A)*	−0.027	O(3A)*	0.044	O(5A)*	−0.013
O(2A)*	−0.014	O(4A)*	0.021	O(6A)*	0.047
C(22A)*	−0.137	C(24A)*	0.399	C(26A)*	0.333
C(23A)*	0.020	C(25A)*	0.502	C(27A)*	0.331
Molecule *B*					
C(1B)	−0.006	C(8B)	0.001	C(15B)	0.005
C(2B)	0.076	C(9B)	0.011	C(16B)	0.004
C(3B)	0.000	C(10B)	−0.009	C(17B)	−0.007
C(4B)	−0.001	C(11B)	−0.005	C(18B)	0.001
C(5B)	0.011	C(12B)	0.016	C(19B)	0.009
C(6B)	−0.003	C(13B)	−0.014	C(20B)	−0.012
O(1B)*	−0.006	O(3B)*	−0.030	O(5B)*	−0.10
O(2B)*	−0.032	O(4B)*	−0.026	O(6B)*	0.027
C(22B)*	−0.487	C(24B)*	−0.572	C(26B)*	0.012
C(23B)*	−0.445	C(25B)*	−0.548	C(27B)*	0.018

* Atoms which are not included in the calculation of equations of the planes.

one acetone molecule inside the common cavity giving rise to the molecular capsule. Guest molecules are placed on the inversion center or more precisely an inversion center is in the middle of the line joining the methyl groups of the acetone molecule. Therefore they are disordered in two positions. Acetone molecules are located by such manner that their methyl groups are embedded exactly to the cavities of the facing host molecules. A mean plane of the acetone molecule is parallel to the C(8B)–C(13B) benzene ring (respective angle is equal to 2°). Guest molecules are H-bonded to both CTV molecules by means of bonds O(1G)···H–C(24B)H_2 and O(1G) ··· H–C(25B)H_2 and incorporate facing CTV molecules to form centrosymmetric dimers (Figure 2). It should be noted that a third weaker H-bond also may be considered, namely, H-bond O(1G) ··· H–C(23B)H_2 (Table IV).

Table IV. Intermolecular H-bonds in the structure of the CTV-acetone 4 : 1 complex

Bonds	Symmetry	C · · · O (Å)	C–H (Å)	H · · · O (Å)	∠C–H · · ·O (°)
C(24B)–H · · · O(1G)	x, y, z	3.253	0.92	2.40	155
C(25B)–H · · · O(1G)	$-x, -y, 1-z$	3.337	0.97	2.47	149
C(23B)–H · · · O(1G)	x, y, z	3.401	0.91	2.61	146
C(3A)–H · · · O(4B)	$1+x, 0.5-y, -0.5+z$	3.424	1.04	2.39	170

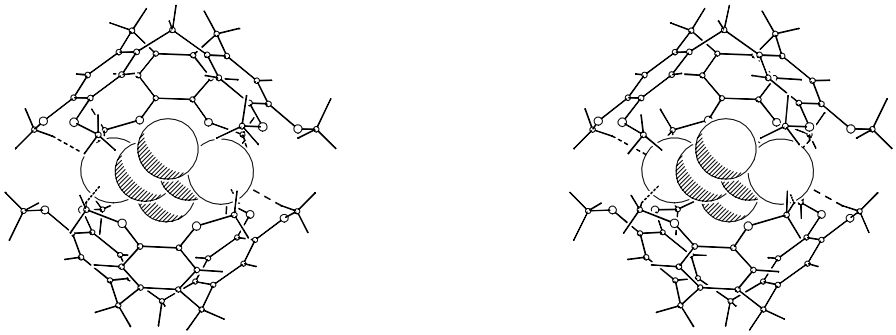


Figure 2. CTV-acetone 2 : 1 endocyclic associate in the CTV-acetone 4 : 1 complex.

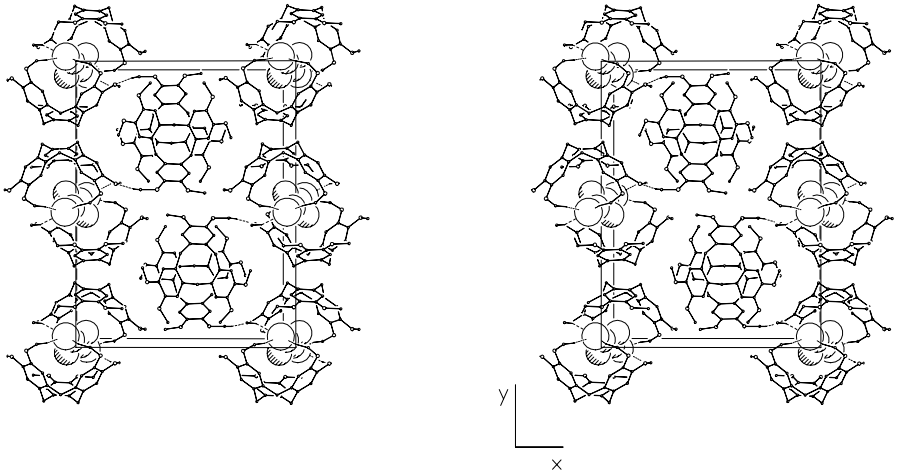


Figure 3. The structure of the CTV-acetone 4 : 1 complex.

Molecules *A* and *B* are associated by H-bonds O(2)-C(23A)H_2–H $\cdots$ O(4)–C(25B)H_3. As a result of this interaction tetramers consisting of the 2 : 1 host-guest dimers and two CTV molecules *A* H-bonded to them are formed. Stacking of these centrosymmetric tetramers gives rise to columns parallel to the direction of the z-axis. The crystal structure is formed as result of packing of these columns (Figure 3).

4. Conclusions

As a result of the crystallization of CTV from its solution in acetone at 40°C a new 4 : 1 host-guest endocomplex, instead of the known 2 : 1 exocomplex, is formed. It may be anticipated that some other guest molecules are also able to form clathrates of this group. Therefore this type of clathrate may be identified as a new group of complexes which are intermediate between CTV host-guest complexes

and its unsolvated forms similar to the 2 : 1 complex between 1,1′-binaphthyl-2,2′-dicarboxylic acid and ethanol [16].

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