Freeze-Fracture Electron-Microscope Observations of the Blue Phase III

J. A. N. Zasadzinski, S. Meiboom, M. J. Sammon, and D. W. Berreman
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 28 March 1986)

Transmission-electron microscopy of chiral 4-(2-methylpentylphenyl)-4′-hexyloxybenzoate (CE4) quenched from its cholesteric and blue phases (BP) I and III are presented. Images of cholesteric and BP I are consistent with an earlier study of similar compounds. CE4 quenched from its BP III is a spaghettilike tangle of filamentary objects of 10- to 50-nm diameter and lengths of 0.1 to 1 μm. These are likely double-twist cylinders in a liquidlike arrangement, melted from their lattice structure in the BP I and II. BP III apparently has a basic, double-twisted structure whose sense and length scale correspond to BP I and BP II, but without the latter's long-range periodicity.

PACS numbers: 61.30.Eb, 64.70.Md

Many cholesteric liquid crystals exhibit from one to three blue phases (BP I, BP II, BP III) over a narrow temperature range (≈ 1 K) near the cholesteric-isotropic transition. Optical measurements[1] have shown that the lower-temperature phases, BP I and II, have cubic structures (of O^8 and O^2 symmetry, respectively) based on a lattice arrangement of double-twist cylinders separated by disclinations.[2] Optical,[1,3] heat-capacity,[4] and elastic-moduli measurements[4] have shown that the highest-temperature blue phase, BP III (also known as the blue fog), is thermodynamically stable, optically active like BP I and II, but visually amorphous.[3] Most of the isotropic-cholesteric latent heat is released in the transition isotropic → BP III, indicating that the BP III is molecularly ordered.[4] The mechanical properties of BP III evolve continuously from being similar to the cholesteric phase at the BP II → BP III transition to being similar to the isotropic phase at higher temperatures.[4] This suggests, as do optical rotatory-dispersion measurements,[5] that, like BP I and II, BP III is locally composed of double-twist cylinders and disclination lines, but the lattice arrangement present in the BP I and II has broken down and these structural units have lost their long-range three-dimensional positional order. Marcus hypothesized that BP III was the "liquid" version of the "crystalline" BP I and II.[3] A Landau calculation by Hornreich, Kugler, and Shtrikman of the stability of a single double-twist cylinder has relevance to this model.[6] More recent Landau-theory calculations by Hornreich and Shtrikman[7] and Rokhsar and Sethna[8] have considered the possibility of an icosahedral ordering of the molecules in the BP III, although the results of the calculations are inconclusive.

To attempt to clarify the structure of BP III we have used freeze-fracture electron microscopy to obtain direct images of the cholesteric and blue phases of CE4.[9] From optical microscopy, CE4 is observed to have the following transition temperatures (in degrees Celsius):

$$\text{cholesteric} \xrightarrow{36.0} \text{BP I} \xrightarrow{36.5} \text{BP III} \xrightarrow{37.1} \text{isotropic.}$$

The reflection wavelengths in the BP III of CE4 are difficult to see because they are of short wavelength. It is possible, however, to confirm that the BP III is present by slightly rotating the polarizer around the apparent extinction point in transmission. Because the rotation of the plane of polarized light is wavelength dependent,[3,5] BP III appears blue when the polarizer is rotated toward one side of extinction, and pink on the other. This effect disappears in the isotropic phase; when the polarizer is rotated one way or the other, it appears gray. The BP I is nucleated as small platelets over about an hour from the BP III at a temperature of several tenths of a degree below the BP-III → BP-I transition. It is impossible to say that no microscopically small platelets were nucleated immediately on cooling; however, it was clear that a significant fraction of the BP III remained for several hours on cooling. The BP I supercools a few degrees before slowly transforming into the cholesteric phase. We never observed the isotropic → BP-III transition to supercool. In all cases, the extent of supercooling depended on the cooling rate.

To prepare a liquid-crystalline phase for freeze fracture, it must be quenched rapidly enough that the desired phase supercools and is frozen in place.[10] Ideally, one would like to induce a step change in temperature from that of the appropriate phase to cryogenic temperatures. In practice, of course, this is impossible. The technique used here to enhance rapid quenching is the double-replica method. A 0.1–0.5-μl droplet of CE4 was trapped between two copper planchettes (Balzers BUO-12-056T; Hudson, New Hampshire) to form a 10–50-μm-thick layer. The sample sandwich was placed in a Mettler variable-temperature microscope stage next to a sample of material between two cover-glass slides. The latter sample was observed through the polarizing microscope. At the appropriate temperature, the desired phase was visually observed and the copper sandwich was quickly dropped into a liquid propane bath cooled to $-190\,^{\circ}$C by liquid nitrogen. Average cooling rates are estimated to be 5000 °C/sec, although initial rates are much

FIG. 1. Transmission-electron microscopy image of a freeze-fracture replica of CE4 (Ref. 9) quenched from the helical cholesteric at 34 °C to − 190 °C. The pitch is 240 nm.

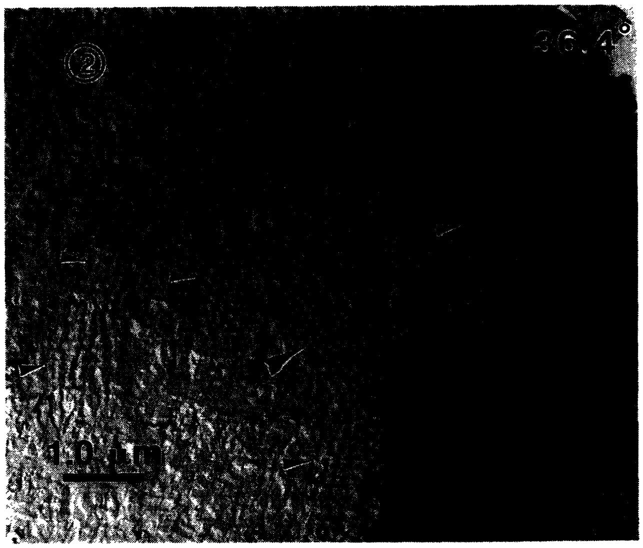

FIG. 2. As Fig. 1 except that CE4 was quenched from the BP I at 36.4 °C. The small arrows point out square patterns along a {100} plane. The large arrow points toward a regular zigzag pattern. The two-dimensional periodicity is expected from the lattice structure of the BP I.

lower.[11] The frozen specimens were fractured at − 170 °C and 10^{-8} Torr in a Balzers 400 freeze-etch apparatus. The fracture surfaces were replicated with 1.5 nm of platinum evaporated at a 45° angle, followed by 15 nm of carbon deposited normal to the fracture surface to increase mechanical strength.

In our experience, it is possible to quench only those phases that supercool to some extent. The cholesteric and BP I of many chiral compounds supercool readily[1,3,4] and have been freeze fractured successfully.[10] BP II, which does not supercool, has never been successfully quenched. Although the nature of the isotropic → BP-III transition is not well understood, it is continuous and does not supercool[4]; hence it is difficult to quench successfully. The phase behavior and properties of the blue phases of CE4 make it an ideal material for freeze-fracture imaging of the BP III. The temperature range of the BP III is exceptionally large, about 0.6 °C, and the compound readily supercools. As previously mentioned, the BP I is nucleated as small platelets over several hours out of the BP III at a temperature of several tenths of a degree below BP III → BP I transition. The BP I supercools a few degrees before slowly transforming into the cholesteric phase. Because the blue phases are near room temperature, they are not significantly precooled during their brief exposure to room-temperature air during the plunge from the Mettler stage into the propane bath.

Figure 1 is an image of the fracture surface of CE4 quenched from the helical cholesteric phase at 34.0 °C and shows the one-dimensional periodic structure expected for this phase. Each light-line–dark-line pair corresponds to one-half pitch of the helix. The pitch is about 240 nm, in good agreement with optical measurements. Figure 2 shows the fracture surface of CE4 quenched from the BP I at 36.4 °C. The small arrows point out square patterns corresponding to fracture along a {100} plane of the cubic lattice.[10] At the large arrow, a regular zigzag pattern is visible that is caused by a more complicated, unknown fracture plane. These areas show a regular periodicity in two directions, as expected from the lattice structure of the BP I. Both cholesteric and BP I images of CE4 are consistent with corresponding images of similar compounds in an earlier study.[10]

Figures 3(a) and 3(b) show CE4 fracture surfaces quenched from the BP III at 36.6 °C. The observed textures are quite different from either the cholesteric (Fig. 1) or BP I (Fig. 2) fracture surfaces. The surface in Fig. 3(a) appears to be covered by filamentary-shaped objects of varying diameter between 10 and 50 nm packed in a random fashion. Small groups of filaments extend for 0.1–1.0 μm in a given direction, before either ending or changing direction. When fractured obliquely to the filament axes, the surface appears as an irregular array of bumps and pits as shown in the upper left-hand side of Fig. 3(b). These cylindrically shaped objects are most likely the double-twist cylinders also present in the BP I and II, but here arranged in a random, liquidlike fashion as suggested by Marcus.[3] This is likely because a material fractures more easily through the disordered disclinations separating the double-twist cylinders than

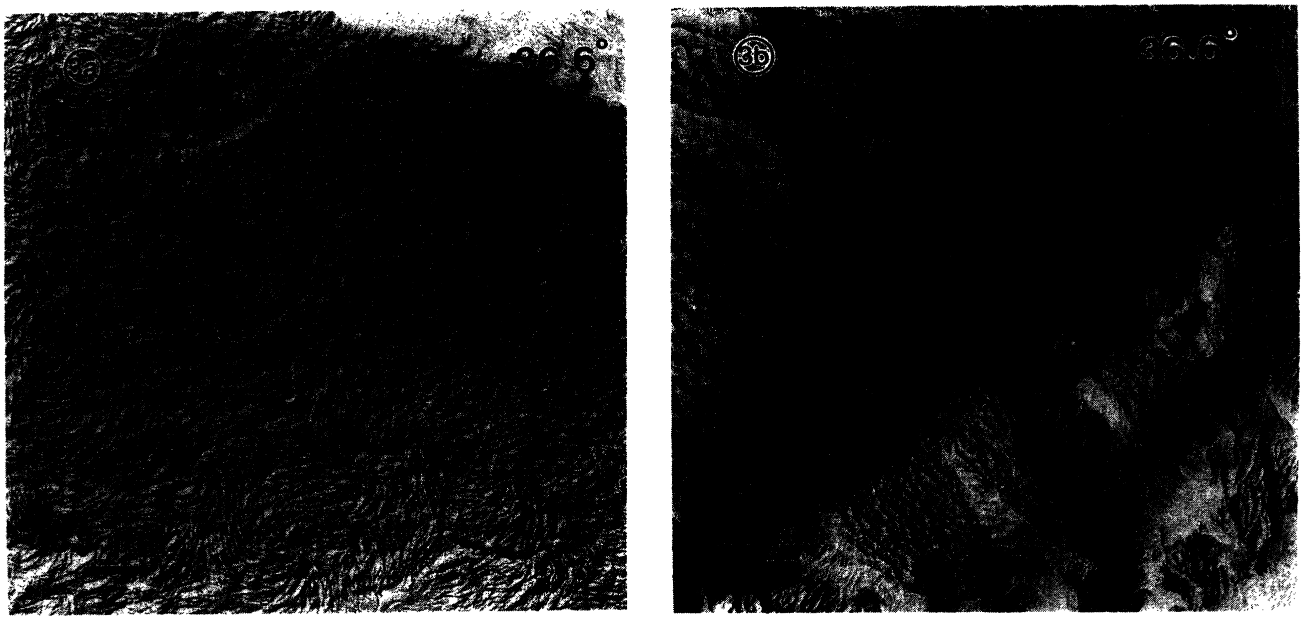

FIG. 3. (a) As Fig. 1 except quenched from BP III at 36.6 °C. Irregular filamentous structure is indicative of a melted lattice of double-twist cylinders. (b) A different area of the same sample as (a), showing oblique fracture of double-twist cylinders.

through the well-ordered double-twist cylinders themselves.[12] These double-twist cylinders are only a fraction of the cholesteric pitch in diameter, much smaller than those believed to exist in the BP I.[1-4] The mechanical measurements of Kleiman *et al.*, however, suggest that the double-twist cylinders in BP III should be smaller in diameter than in BP I.[4] No long-range periodicity was observed, although the double-twist cylinders appear to be aligned with their neighboring cylinders in a nematic fashion. The overall impression is that of a tangled, spaghettilike network of cylinders of various diameters and lengths that are locally parallel.

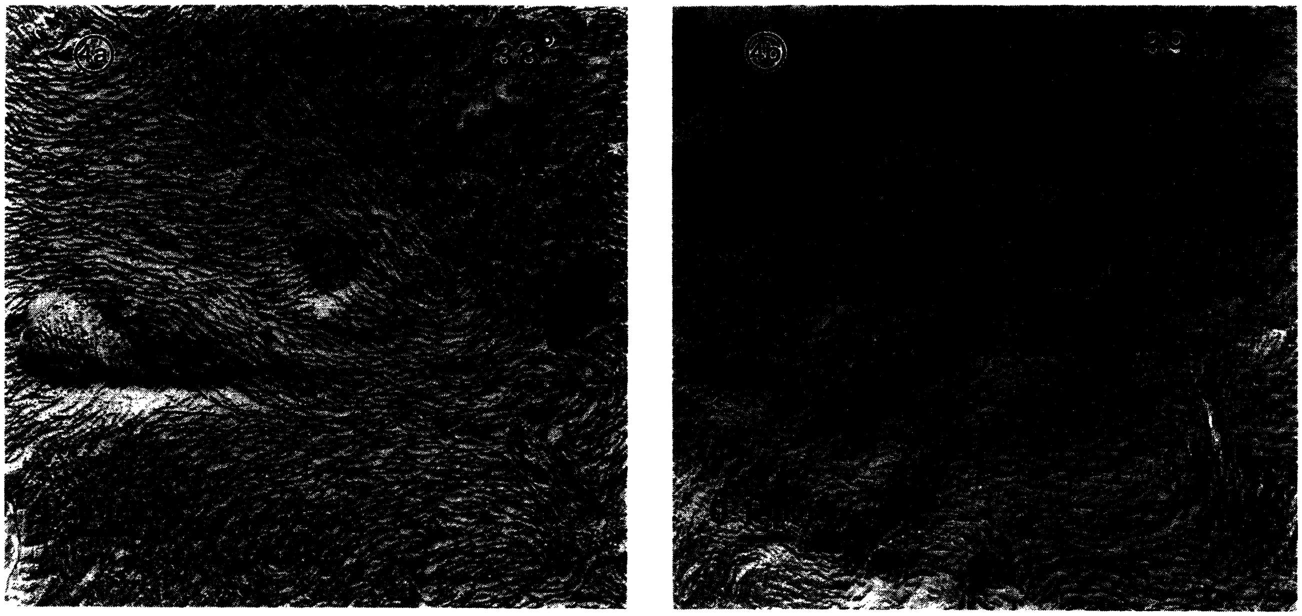

FIG. 4. (a) As Fig. 3(a), but nominally quenched from the isotropic at 38 °C. Slow initial cooling rates of the double-replica technique (see text) cannot trap CE4 as an isotropic liquid this close to the continuous transition from the isotropic to BP III. (b) As (a) except quenched from 39 °C. BP-III texture is observed. The isotropic to BP-III transition can only be avoided by starting the quench from > 45 °C (see text).

Figures 4(a) and 4(b) show CE4 fracture surfaces quenched from the isotropic liquid at 38 and 39 °C, respectively (≈ 1–2 °C above the BP-III → isotropic transition). These figures show similar textures to those quenched from the BP III at 36.6 °C (Fig. 3). Although nominally quenched from the isotropic, the actual phase locked in by the freezing process is most likely still the BP III. The isotropic → BP-III transition is continuous[4] and the initial cooling rate is presumably too low for supercooling to occur.[10] When the isotropic material is quenched from 45 °C and the cooling rate at the transition is higher, a featureless fracture surface is obtained, devoid of any of the spaghettilike textures present in Figs. 3 and 4.

These freeze-fracture images provide a unique, real-space view of supramolecular order in the cholesteric and blue phases unavailable by any other technique. They show that the BP III of CE4 is a spaghettilike tangle of double-twist cylinders of diameters a fraction of the cholesteric pitch. No long-range structure or periodicity is present, although the double-twist cylinders appear aligned over distances of a few microns. The lattice structure of the BP I and II apparently breaks down in the BP III, leaving a liquidlike arrangement of locally double-twisted regions. BP III apparently has a basic, double-twisted structure whose sense and length scale correspond to BP I and BP II, but without the latter's long-range periodicity. These conclusions are consistent with the results of previous optical, heat-capacity, and mechanical measurements on BP III. We are attempting to develop a theory of the fracture process for rapidly quenched liquid-crystalline materials to relate the observed fracture behavior directly to the local molecular structure.[12]

We would like to thank M. Marcus for bringing CE4 to our attention and for many helpful suggestions on the BP III. We are also grateful for helpful discussions with R. Pindak.

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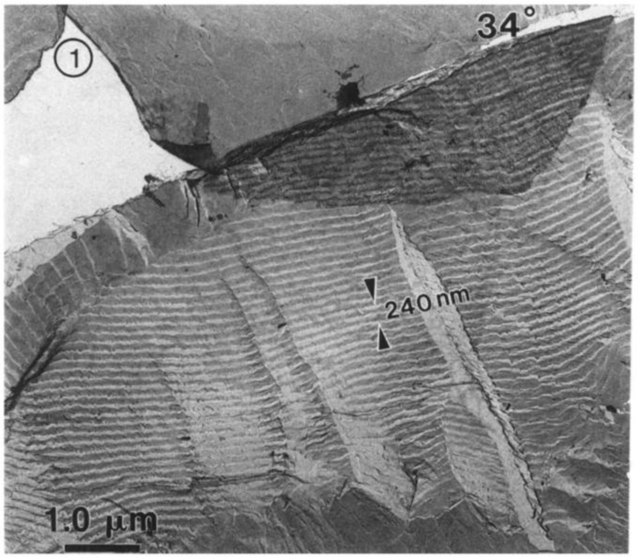

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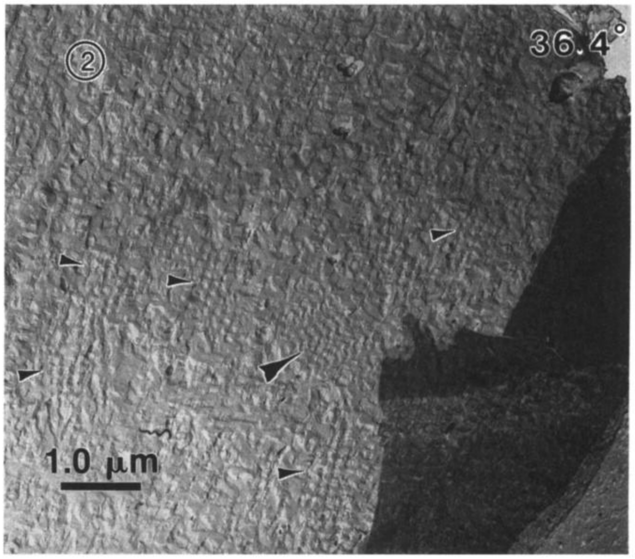

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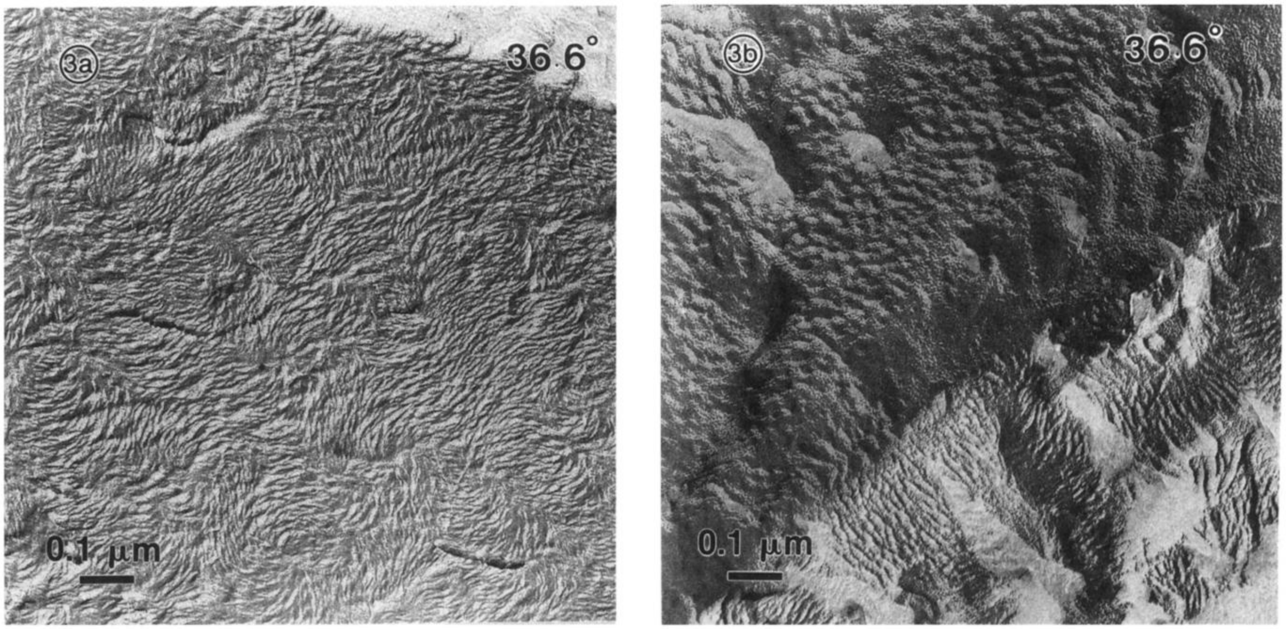

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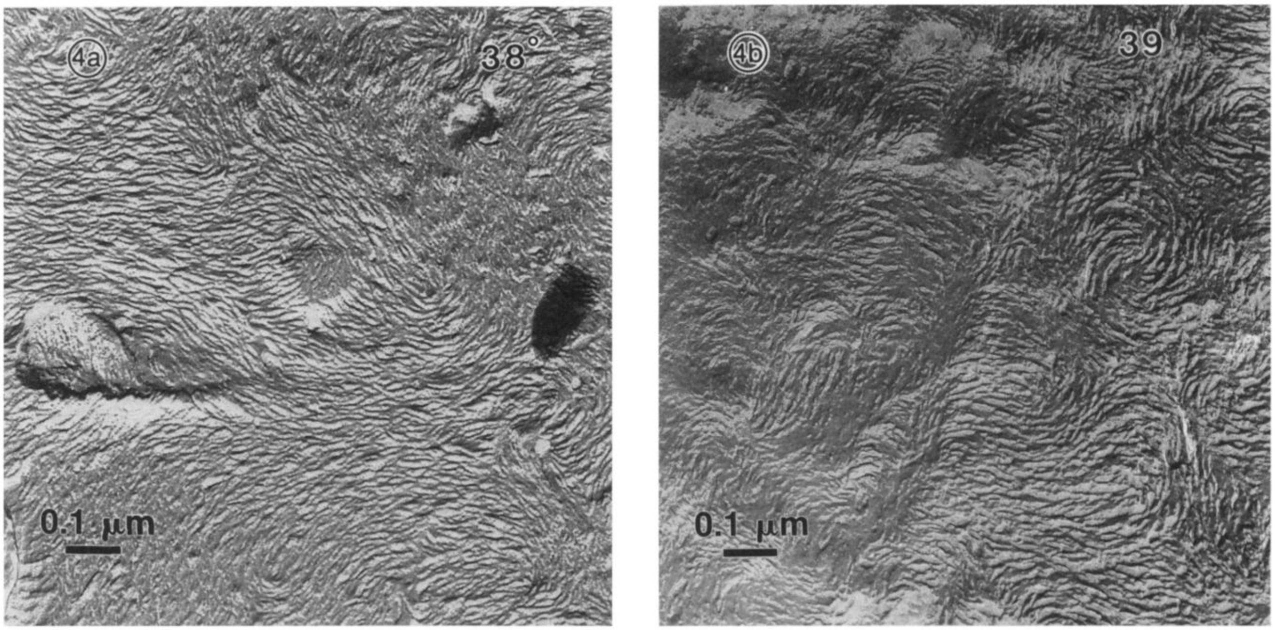

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