Rotor–stator molecular crystals of fullerenes with cubane

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Cubane[1] (C_8H_8) and fullerene[2] (C_{60}) are famous cage molecules with shapes of platonic or archimedean solids. Their remarkable chemical and solid-state properties have induced great scientific interest[3–5]. Both materials form polymorphic crystals of molecules with variable orientational ordering[6–9]. The idea of intercalating fullerene with cubane was raised several years ago[10] but no attempts at preparation have been reported. Here we show that C_{60} and similarly C_{70} form high-symmetry molecular crystals with cubane owing to topological molecular recognition between the convex surface of fullerenes and the concave cubane. Static cubane occupies the octahedral voids of the face-centred-cubic structures and acts as a bearing between the rotating fullerene molecules. The smooth contact of the rotor and stator molecules decreases significantly the temperature of orientational ordering. These materials have great topochemical importance: at elevated temperatures they transform to high-stability covalent derivatives although preserving their crystalline appearance. The size-dependent molecular recognition promises selective formation of related structures with higher fullerenes and/or substituted cubanes.

High-symmetry molecular solids are not only for aesthetic curiosity; the simple physical and chemical properties of these structures make possible a better understanding of intermolecular interactions in the low-symmetry analogues. Most of the ionic derivatives of fullerenes represent high-symmetry structures[11], but in heteromolecular crystals the interactions with the low-symmetry components usually destroy the face-centred-cubic (f.c.c.) lattice of fullerenes[12]. Owing to its cubic shape and suitable size, cubane is a promising candidate for forming a high-symmetry heteromolecular crystal with C_{60}. At the same time, the high chemical reactivity of the constituents predicts solid-state chemical reactions at elevated temperatures.

We prepared stoichiometric $C_{60} \cdot C_8H_8$ and $C_{70} \cdot C_8H_8$ solids from aromatic solutions of fullerenes and cubane by evaporating the solvent or adding isopropyl alcohol as a precipitant. Octahedral or platelet-shaped crystals were formed with typical sizes of 5–200 µm, depending on the rate of precipitation. The crystals are soluble in toluene; their high-performance liquid chromatography analysis confirms 1:1 stoichiometry. The infrared spectra consist of the characteristic lines of fullerenes and cubane without any shift, reflecting weak van der Waals interactions between the molecules (see Supplementary Information, Fig. S3).

The crystal structures were determined by X-ray diffraction. Identical results on powders and single crystals indicated that the various batches were homogenous and reproducible. The cubane derivatives of fullerenes have several polymorphic structures with phase transitions and irreversible chemical reactions. We summarize the most important properties as a function of temperature (T) in a schematic phase diagram (Fig. 1). At ambient temperature the crystal structure of C_{60}–cubane is f.c.c. (see Supplementary Information, Fig. S1). C_{60} molecules rotate freely at the lattice sites whereas orientationally ordered cubanes occupy the octahedral voids in between (Fig. 2a). The cubes of cubane, aligned parallel with the faces of the unit cell, are in a higher symmetry environment than in their pure crystals[13]. C_{60} forms an f.c.c. sublattice, similar to its parent structure[6,7], but with nearest-neighbour distances increased from 10.01 to 10.42 Å. Owing to the significantly expanded lattice, C_{60} molecules do not form an interconnected framework; instead the structure is stabilized by the fullerene–cubane interactions. We explain the strong fullerene–cubane attraction as a molecular recognition between convex and concave surfaces. Figure 2b illustrates the position of cubane inside an octahedral void. The concave faces of the octahedral void, carved out by neighbouring C_{60} balls, perfectly wrap the faces of the cubane. Such a match of complementary surfaces, that is, molecular recognition, can maximize the attractive forces between C_{60} and cubane and stabilize the structure, compensating for the weaker interfullerene interactions. Although molecular recognition allows the rotation of C_{60}, it keeps cubane in the equilibrium position and orientation. ^{1}H NMR measurements confirm unambiguously the static character of
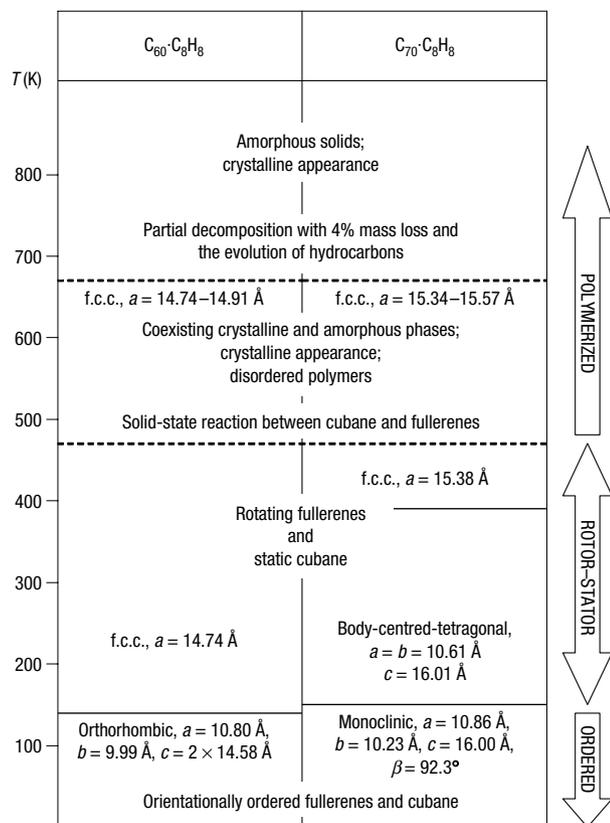
	$C_{60} \cdot C_8H_8$	$C_{70} \cdot C_8H_8$
	Amorphous solids; crystalline appearance	
	Partial decomposition with 4% mass loss and the evolution of hydrocarbons	
	f.c.c., a = 14.74–14.91 Å	f.c.c., a = 15.34–15.57 Å
	Coexisting crystalline and amorphous phases; crystalline appearance; disordered polymers	
	Solid-state reaction between cubane and fullerenes	
		f.c.c., a = 15.38 Å
	Rotating fullerenes and static cubane	
	f.c.c., a = 14.74 Å	Body-centred-tetragonal, $a = b$ = 10.61 Å c = 16.01 Å
	Orthorhombic, a = 10.80 Å, b = 9.99 Å, $c = 2 \times 14.58$ Å	Monoclinic, a = 10.86 Å, b = 10.23 Å, c = 16.00 Å, β = 92.3°
	Orientationally ordered fullerenes and cubane	

T (K): 800, 700, 600, 500, 400, 300, 200, 100

POLYMERIZED / ROTOR–STATOR / ORDERED

Figure 1 Schematic phase diagram of the fullerene–cubane solids.

cubane: the wide spectrum line with fine structure characteristic of multispin systems remains unchanged within a temperature range of 130–381 K. The measured second moment of the spectrum agrees excellently with the calculated value for static cubane molecules (see Supplementary Information, Fig. S5). Thus, cubane acts as a molecular bearing for the rotating fullerenes. The alternating array of rotating and static molecules is a characteristic feature of this 'rotor–stator' phase and different from both orientationally ordered and plastic crystals. A further result of molecular recognition is an effective space filling: in spite of the expanded lattice, the volume of the heteromolecular crystal is less than the sum of its components[7,13].

The closest kin of the above rotor–stator phase is the f.c.c. C_{70}–cubane above 390 K (Fig. 1). This structure can be derived from the high-temperature phase of pure C_{70} (ref. 14), with the octahedral voids filled again by orientationally ordered cubane. Owing to the larger size of the freely rotating C_{70} balls, the lattice expansion is smaller for C_{70}–cubane than for C_{60}–cubane. It is instructive to compare the size of the expanded lattices with their parent structures. The lattice parameter of the rotor–stator crystals is the sum of the effective diameter of fullerenes and the size of cubane along the cubic cell edges. For the latter we obtain 4.74 Å, independently of the diameter of the actual fullerene. Applying the same argument, the expected lattice expansion is even less for higher fullerenes. At a threshold ball diameter of 11.44 Å, cubane can occupy the octahedral voids without any lattice expansion, that is, the material becomes a true host–guest compound. At this size the influence of molecular recognition, combined with optimal interfullerene interactions, may give rise to the formation of crystals with high stability. On the basis of the lattice parameter[15],
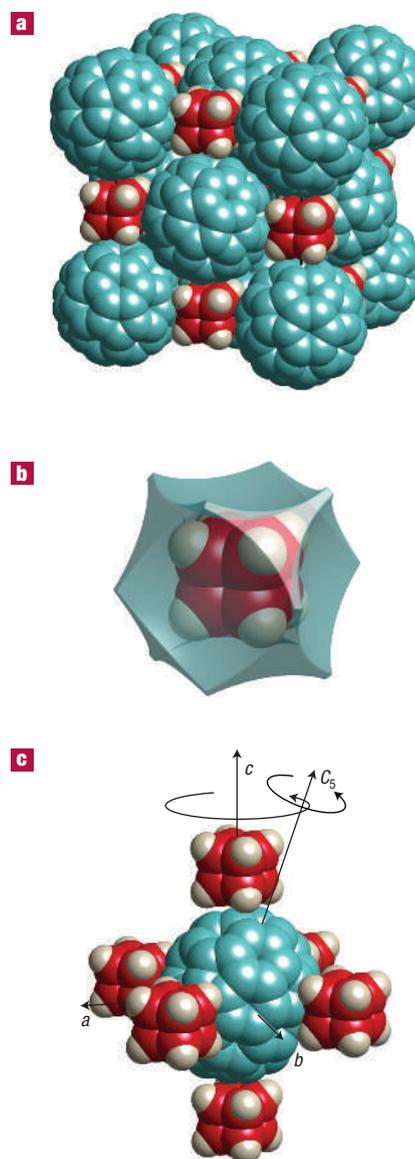

Figure 2 Structure of the fullerene–cubane heteromolecular crystals. **a**, A space-fill view of the rotor–stator phase of $C_{60} \cdot C_8H_8$. Rotating fullerenes occupy the f.c.c. lattice sites and static cubanes are in the octahedral voids in between. **b**, The position of cubane in an octahedral void of the f.c.c. cell. Concave outer faces show the perfect match between cubane and the surrounding fullerenes. **c**, The restricted motion of C_{70} in the tetragonal rotor–stator phase of $C_{70} \cdot C_8H_8$. In the molecular bearing of six cubanes, C_{70} rotates about its long axis (C_5), which precesses about the c axis of the body-centred-tetragonal cell.

C_{84} and fullerenes of similar size may be good precursors for such compounds.

On cooling, the rotor–stator phases undergo orientational-ordering phase transitions (Fig. 1). In C_{60}–cubane this takes place at around 140 K. The phase transition is reflected by the lowering of the crystal symmetry from f.c.c. to orthorhombic. In C_{70}–cubane two phase transitions occur: one at 390 K and another at 150 K (Fig. 1). On cooling the crystal, the symmetry changes from f.c.c. to body-centred tetragonal at 390 K (see Supplementary Information, Fig. S2). At this point free rotation of the C_{70} molecules becomes restricted. The basic motion is a uniaxial rotation about the long molecular axis (C_5). In addition,
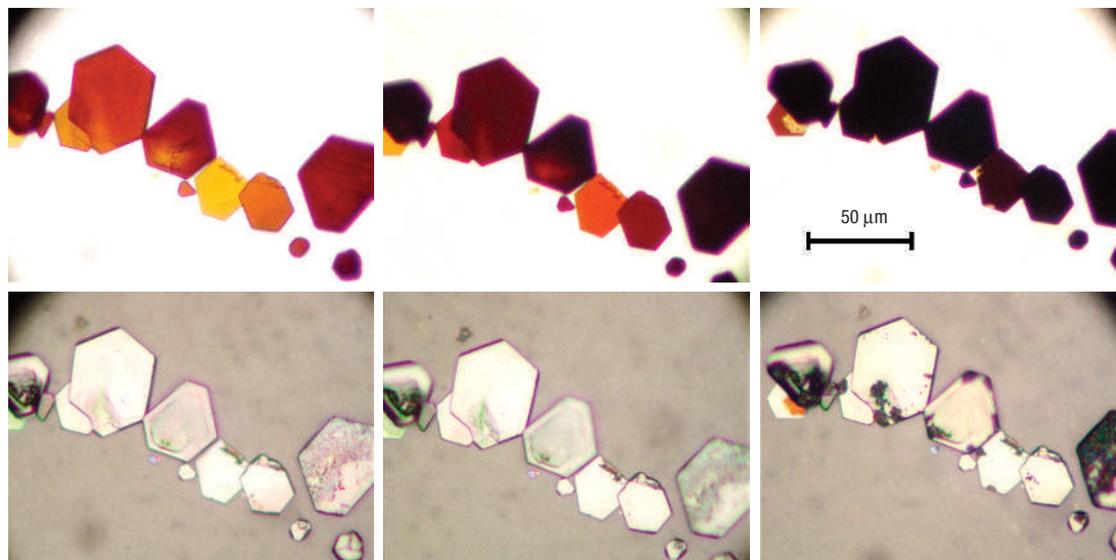
Figure 3 **The influence of heat treatment on the appearance of C$_{60}$·C$_8$H$_8$ single crystals.** Transmission (top) and reflection (bottom) optical micrographs of crystals precipitated onto a quartz plate. Left: pristine rotor–stator crystals; middle: crystals polymerized for 1 h at 520 K; right: crystals partially decomposed by subsequent heat treatment for 1 h at 870 K.

the axis of rotation also moves, precessing about the c direction of the tetragonal unit cell with a full opening angle of 40° (Fig. 2c). Cubane molecules occupy the axially elongated octahedral positions and are orientationally ordered. As the anisotropy can be attributed to the shape of C$_{70}$, the local environment of cubane molecules remains similar to that found in the f.c.c. lattice (Fig. 2b). This structure is also stabilized by molecular recognition and the restricted rotation of C$_{70}$ molecules does not affect the rotor–stator character. In the plastic crystalline phases of pure fullerenes the repulsive π–π interactions of neighbouring molecules give rise to the orientational-ordering phase transitions[7]. In the present rotor–stator crystals these interactions are minimized by the increased interfullerene distances. On the other hand, the match with the six surrounding cubane molecules facilitates a smooth rotation of fullerenes. This influence of molecular bearing may be responsible for the unusually low phase-transition temperatures (140 and 150 K). Further studies are needed to reveal the detailed structure of the low-temperature phases.

The high-temperature behaviour of these compounds is also special: on heating to 470 K in vacuum, the heteromolecular crystals transform to high-stability covalent derivatives. The following experiments prove solid-state chemical reactions: during heat treatment of a few hours the infrared spectra change significantly, cubane peaks vanish and new peaks, characteristic of fullerene adducts, appear simultaneously (see Supplementary Information, Fig. S3). At the same time the chemical composition remains unchanged as shown by thermogravimetry mass spectrometry (see Supplementary Information, Fig. S4). The final products are insoluble in all solvents of fullerenes, for example, toluene and o-dichlorobenzene. Both C$_{60}$ and C$_{70}$ derivatives transform at 470 K. Around this temperature pure cubane isomerizes to more stable C$_8$H$_8$ hydrocarbons through reactive intermediates[16,17]. We assume that the surrounding fullerenes open different routes for the isomerization of cubane and form addition compounds, probably copolymers with the intermediates. Owing to the chemical reaction the materials become predominantly amorphous with residual crystalline phases of increased lattice parameter (Fig. 1). Surprisingly, these structural changes have

hardly any influence on the macroscopic appearance of the crystals (Fig. 3): they retain the shiny, flat faces with sharp edges, only the colour of the thin transparent crystals becomes deeper. The amorphous phase is consistent with a random polymerization in the precursor f.c.c. lattice. On the other hand, the coexistence of two phases without destroying the single crystals indicates that the volume does not change significantly. On further heating, thermal decomposition takes place in the 670–870 K range, accompanied with 4% mass loss in the form of toluene, benzene, acetylene, ethylene and methane (see Supplementary Information, Fig. S4). No evaporation of fullerenes is observed, showing that the materials are still polymerized. It is remarkable that after these drastic heat treatments the macroscopic habit of the materials seems crystalline (Fig. 3): the significantly darker 'crystals' retain their shiny, flat faces. These important observations demand further research to reveal the microscopic nature of the solid-state reactions of fullerenes with cubane.

C$_{60}$–cubane and C$_{70}$–cubane are the first members of a family of rotor–stator crystals. These high-symmetry structures have promising properties for future applications. The components are held together by a perfect match between convex and concave molecular surfaces. Further study of this simple molecular recognition may help to understand similar interactions between molecules of more complex shapes. We found that cubane expands the lattice of fullerenes, depending on their size. This size recognition predicts the formation of more stable derivatives of higher fullerenes, and may be used in their size-selective separation. At the same time, the increased size of tetrahedral voids may incorporate ions or molecules too large for the original fullerene structures. The conditions of molecular recognition may be satisfied in functionalized fullerenes and cubanes, extending the family of related materials. In contrast to both orientationally ordered and plastic crystals, these materials consist of distinct rotor and stator components. As fullerenes rotate freely in the bearing of cubanes, we predict that surface functionalized derivatives can be the precursors of future molecular motors. Thermal solid-state reactions change the solubility and optical absorptivity of the fullerene–cubane materials, although preserving

their macroscopic crystalline appearance. These properties may be used in photolithographic applications.

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