

A New Phase of Crystalline Anthracene: Its Importance in Solid-state Photodimerization

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Summary A metastable phase of anthracene, which smoothly dimerizes upon u.v. irradiation, has been identified, and its crystal structure determined, by an electron microscopic and computational approach.

We report the discovery of a new metastable phase of crystalline anthracene, the identity of which has been

established by a combined use of micro-electron diffraction, computations involving pairwise interaction between non-bonded atoms, and a model-building approach using van der Waals radii. The new phase may be readily produced at room temperature by application of a compressive force perpendicular to the (001) (*i.e.* basal) planes of single crystals of the thermodynamically stable ($P2_1/a$) form of anthracene

I. The transformation into the new, triclinic phase II proceeds rapidly in single crystal \rightarrow single crystal fashion, the topotactic relationship being $(001)_I \parallel (001)_{II} \parallel (10\bar{1})_I \parallel (100)_{II}$ and $(011)_I \parallel (010)_{II}$. On the basis of the approximate unit cell parameters derived from diffraction analysis, the well known¹ atom-atom pairwise approach permits a refined structure to be computed. It transpires that the space group is $P1$ with $a = 8.312$, $b = 6.306$, $c = 11.035$ Å, $\alpha = 123.69$, $\beta = 101.29$, and $\gamma = 89.5^\circ$; $U = 468.39$ Å³, $Z = 2$. This structure is estimated (by calculation¹) to possess a lattice energy only 5.5 kJ mol⁻¹ less than that of the monoclinic form.

Electron microscopic observations² have indicated that moderate stress produces crystallites of the new phase in coherent contact with the parent crystal matrix in one specific orientation. Subsequent observations, following u.v. irradiation of the stressed specimens, revealed that these crystallites act as nuclei for photochemical dimerization which, in due course, spreads throughout the entire specimen. The existence of these coherent inclusions of anthracene II, having a small lattice mismatch (*ca.* 3%) topotactically oriented within anthracene I, is in line with all the facts brought to light by electron microscopy and diffraction. At the same time it affords direct evidence for the suggestion, made by Ubbelohde,³ that hybrid (biphasic) organic molecular crystals may exist and confirms our earlier observation on substituted anthracene.⁴

Further details, including the mechanism of the photochemical transformation, the photophysical attributes of the excimeric emissions that arise from biphasic specimens, and the atomic co-ordinates of the unit cell contents, will be discussed elsewhere. Of considerable significance, however, is the diminution in C(9) \cdots C(9') distance in proceeding from the $P2_1/a$ to the $P1$ structures. In the monoclinic phase this value is 4.5 Å, well above the value at which it is believed⁵ photodimerization can no longer take place in the solid state, whereas in the new phase the corresponding distance is 4.2 Å. Of equal significance is that, in the triclinic phase, there is enough room for rotation of neighbouring molecules to occur so as to bring them into the overlapped registry necessary for the easy production of the *para*-dimer.

The general importance of stress-induced phase changes in solid-state photochemical processes⁶ is currently under investigation. In this connection it is relevant to note that the symmetric benzoate of hexa-2,4-diyndiol undergoes little polymerization in its thermodynamically stable phase, but is polymerizable by mechanical stress to form an extended-chain polydiacetylene.⁷

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