The Central C-C Bond Length in the Bi(anthracene-9,10-dimethylene) Photoisomer: Unusual Elongation and Crystalline State Reaction

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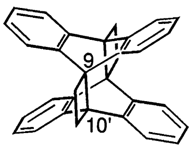
Crystal structure analysis of bi(anthracene-9,10-dimethylene) photoisomer (**1**) revealed that the anomalous elongation of the central C–C bond in the previously reported X-ray structure is an artifact caused by partial cycloreversion of **1** to no-bonded isomer in crystalline state.

The central C–C bond (C9–C10') of the photoisomer (**1**) of bi(anthracene-9,10-dimethylene) (**2**) has been known as one of the longest C(sp^3)–C(sp^3) bonds. Its length was determined to be 1.77(1) Å by Ehrenberg using X-ray diffraction.[1] The anomalous bond elongation provoked great interest among organic and theoretical chemists, and several attempts to rationalize it have been made.[2-4]



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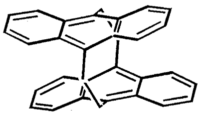


2

Allinger and his co-workers estimated the bond length to be 1.64 Å from the molecular mechanics and the ab initio calculations.[5] They state "it seems clear that the X-ray results are unreliable." Very recently Siegel and his co-workers redetermined the X-ray structure of **1** and showed that the C–C bond length is 1.648(3) Å.[6] This value closely agrees with the structures obtained from HF and DFT calculations.[6] We independently carried out single crystal X-ray diffraction measurements for **1**.[7] This paper discusses the origin of the anomalous bond elongation in the previously reported X-ray structure in terms of crystalline state reactions.

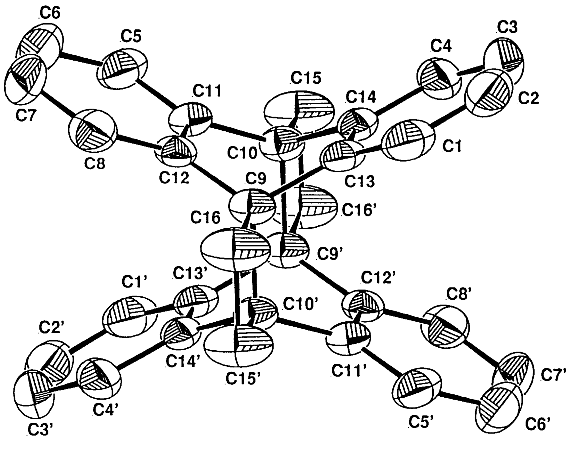
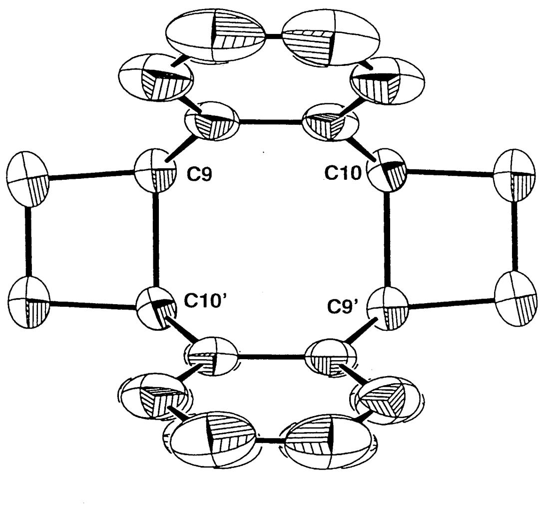


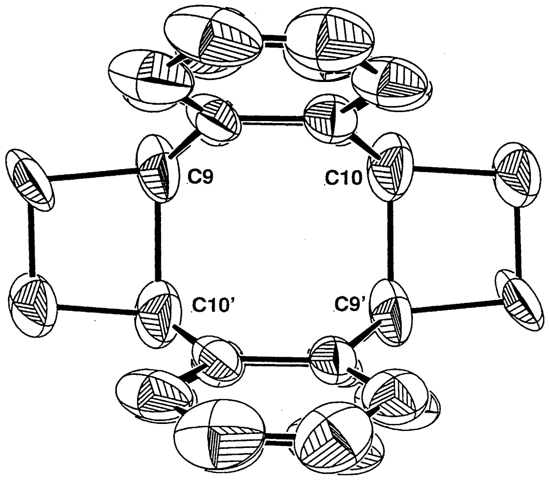
Figure 1. ORTEP drawing of **1** with hydrogen atoms omitted for clarity. The thermal ellipsoids are scaled to the 50% probability level.

The ORTEP diagram is shown in Figure 1. In contrast to Ehrenberg's observation, no significant fluctuation in the intensity of standard reflections was observed during the data collection.

The observed molecular structure (which is referred to as Structure A hereafter) is essentially identical with the structure reported by Ehrenberg (which is referred to as Structure B) except the central C(sp^3)–C(sp^3) bond C9–C10'. Its bond length in Structure A (1.663(4) Å) is considerably shorter than that in



Structure A



Structure B

Figure 2. Side views of Structure A (top) and Structure B (bottom).

Structure B (1.77(1) Å) and agrees fairly well with the length obtained by Siegel and his co-workers.[6] It is therefore established that the true length of the central C(sp^3)–C(sp^3) bond is not 1.77 Å but 1.66 Å.

Now there is a question: Why did the C9–C10' bond appear to become extraordinarily long in Structure B? Our answer is as follows.

Figure 2 shows side views of Structures A and B. A careful inspection of the orientation of the probability density function ellipsoids of C9 and C10' reveals that their longest axes are directed nearly along their interatomic vector in Structure B but not in Structure A. This observation suggests that there would be an unresolved disorder which does not show strong residual peaks in the difference density maps for Structure B. Such a disorder can occur if the isomer **2** coexists in the crystal of **1**.

It has been reported that compound **1** gradually changes into compound **2** in the solid state in the dark.[8] We found that this cycloreversion proceeds with retention of the single crystals: Having been left in the dark for a few months after X-ray diffraction measurements, the piece of the single crystals of **1** changed into a single crystal of **2**, the X-ray structure[9] of which was found out to be identical with that reported by Wada and Tanaka.[10]

In view of these observations, the instability of the crystals reported by Ehrenberg is interpreted in terms of the partial cycloreversion of **1** to **2** during and/or before the data collection of X-ray diffraction intensities. The observed molecular structure was, accordingly, an average of two isomers **1** and **2**. The interatomic distance between C9 and C10' of **2** (2.773(3) Å) is much longer than that of **1**. Even if the population of **2** is much smaller than that of **1**, the observed length of C9–C10' bond would be considerably elongated.

It is therefore concluded that the anomalous elongation of C9–C10' bond of bi(anthracene-9,10-dimethylene) photoisomer (**1**) in the previously reported X-ray structure is ascribed to an unresolved disorder caused by the partial cycloreversion of **1** to **2** in the crystalline state and that the true bond length of C9–C10' is 1.66 Å.

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References and Notes

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7 Crystal data for **1**: $C_{32}H_{24}$, MW = 408.54, monoclinic, space group $P2_1/a$, a = 8.547(2), b = 13.011(2), and c = 9.8839(9) Å, β = 111.968(9)°, V = 1019.3(3) Å^3, Z = 2, ρ_{calcd} = 1.331 gcm^{-3}, Cu $K\alpha(\lambda$ = 1.54184 Å), μ = 0.53 cm^{-1}, T = 296 K; 1500 unique reflections, 1162 with $I > 2\sigma(I)$ were used for the further calculations after Lorentz and polarization correction. The initial parameters of the refinement were taken from the structure determined by Ehrenberg.[1] The structure was refined by full-matrix least-squares method using XTAL system.[11] All the hydrogen atoms were located from difference maps and refined isotropically. All the carbon atoms were refined anisotropically, 193 least squares parameters. $R(R_w)$ = 0.055 (0.069).

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9 Crystal data for **2**: $C_{32}H_{24}$, MW = 408.54, monoclinic, space group $P2_1/a$, a = 8.446(2), b = 12.583(3), and c = 10.105(2) Å, β = 111.77(1)°, V = 997.4(3) Å^3, Z = 2, ρ_{calcd} = 1.36 gcm^{-3}, μ = 0.54 cm^{-1}, T = 90 K; 1448 unique reflections, 1202 with $I > 2\sigma(I)$ were used for the further calculations after Lorentz and polarization correction. The initial parameters of the refinement were taken from the structure of **1**. All the hydrogen atoms were located from difference maps and refined isotropically. All the carbon atoms were refined anisotropically, 193 least squares parameters. $R(R_w)$ = 0.048(0.059).

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