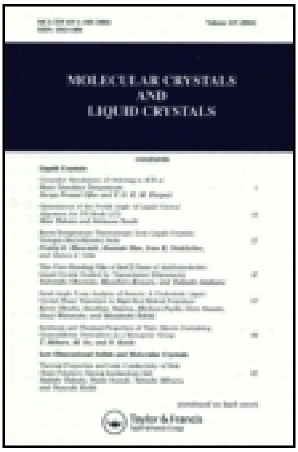


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Central C-C Bond Length in the Bi(Anthracene-9,10-Dimethylene) Photoisomer: Unusual Elongation and Crystalline State Reaction[1]

Jun Harada [a], Keichiro Ogawa [a] & Shuji Tomoda [a]
[a] Department of Chemistry, The College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153

To cite this article: Jun Harada, Keichiro Ogawa & Shuji Tomoda (1996): The Central C-C Bond Length in the Bi(Anthracene-9,10-Dimethylene) Photoisomer: Unusual Elongation and Crystalline State Reaction[1], Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 277:1, 119-123

To link to this article: http://dx.doi.org/10.1080/10587259608046012

Mol. Cryst. Liq. Cryst., 1996, Vol. 277, pp. 119–123
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

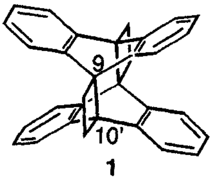
THE CENTRAL C-C BOND LENGTH IN THE BI(ANTHRACENE-9,10-DIMETHYLENE) PHOTOISOMER: UNUSUAL ELONGATION AND CRYSTALLINE STATE REACTION[1]

JUN HARADA, KEIICHIRO OGAWA,* AND SHUJI TOMODA
Department of Chemistry, The College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

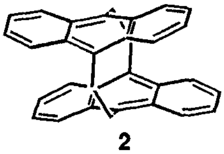
Abstract Crystal structure analysis of bi(anthracene-9,10-dimethylene) photoisomer (**1**) revealed that the anomalous elongation of the central C–C bond in the previously reported X-ray structure is an artifact caused by partial cycloreversion of **1** to no-bonded isomer in crystalline state.

INTRODUCTION

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.[2] The anomalous bond elongation provoked great interest among organic and theoretical chemists, and several attempts to rationalize it have been made.[3-5]



1



2

Allinger and his co-workers estimated the bond length to be 1.64 Å from the molecular mechanics and the ab initio calculations.[6] 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.[7] This value closely agrees with the structures obtained from HF and DFT calculations.[7] We independently carried out single crystal X-ray diffraction measurements for **1**.[8] This paper discusses the origin of the anomalous bond elongation in the previously reported X-ray structure in terms of crystalline state reactions.

RESULTS AND DISCUSSION

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

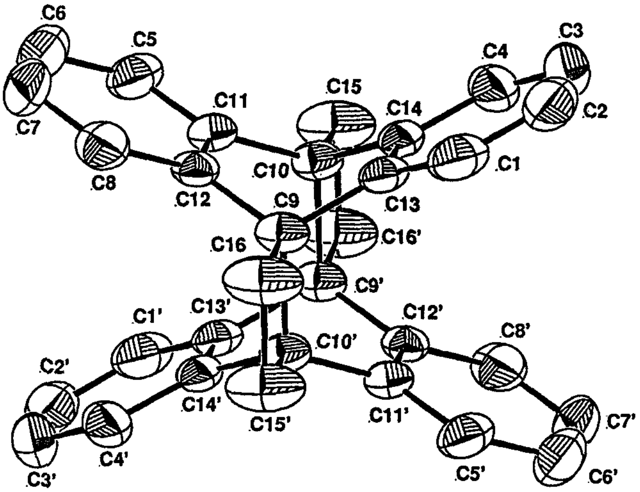


FIGURE I ORTEP drawing of **1** with hydrogen atoms omitted for clarity. The thermal ellipsoids are scaled to the 50% probability level.

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 B (1.77(1) Å) and agrees fairly well with the length obtained by Siegel and his co-workers.[7] 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.

It has been reported that compound **1** gradually changes into compound **2** in the solid state in the dark.[9] 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[10] of which was found out to be identical with that reported by Wada and Tanaka.[11] The ORTEP drawing of **2** is shown in Figure II.

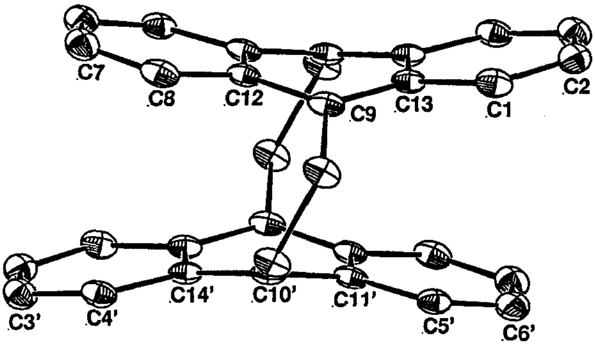


FIGURE II ORTEP drawing of **2** with hydrogen atoms omitted for clarity. The thermal ellipsoids are scaled to the 50% probability level.

The results suggest that isomer **2** could coexist in the crystal of **1** during the cycloreversion reaction. Coexistence of **2** would cause a disorder in the X-ray structure. If the population of **2** is much smaller than that of **1**, the disorder would be unresolvable in difference density maps. However, its effect would appear in the observed molecular geometry. A comparison of geometrical parameters for Structures A and B, and **2** revealed that there was an unresolved disorder ascribable to the coexistence of **2** for Structure B (Table I).

One of the most characteristic differences in the geometry between **1** and **2** is in the arrangement of two anthracene rings within a molecule (See Figures I and II). While in **1** two anthracene rings are arranged nearly symmetrically with respect to a pseudo mirror plane that bisects C9–C10' and C9'–C10 bonds, in **2** they are displaced in the direction along the longest axes of the rings. Thus, in **1** the distance (d_1) between C13 and C14' is equal to that (d_2) between C12 and C11' within experimental error. Similarly the distance (d_3) between C1 and C4' is equal to that (d_4) between C8 and C5' and the distance (d_5) between C2 and C3' is equal to that (d_6) between C7 and C6'. In contrast, in **2**, each of the corresponding distances is distinctly different. Thus, d_1-d_2

amounts to 0.900(5) Å, d_3-d_4 1.242(6) Å, and d_5-d_6 1.345(6) Å. If isomer **2** coexists in the crystal of **1**, it is expected that each of d_1-d_2, d_3-d_4, and d_5-d_6 would have a positive value. This is just the case for Structure B by Ehrenberg.

TABLE I Selected interatomic distances indicating an unresolved disorder due to the crystalline state reaction

	Distances (Å)		
	1 at 296 K (Structure A)	**1** by Ehrenberg (Structure B)	**2** at 90 K
C9–C10' (d_0)	1.663(4)	1.75[a]	2.773(3)
C13–C14' (d_1)	3.744(4)	3.81	4.413(3)
C12–C11' (d_2)	3.733(5)	3.74	3.514(4)
d_1- d_2	0.011(5)	0.07	0.900(5)
C1–C4' (d_3)	6.026(5)	6.01	6.634(3)
C8–C5' (d_4)	6.019(6)	5.94	5.392(4)
d_3- d_4	0.007(8)	0.07	1.242(6)
C2–C3' (d_5)	8.362(6)	8.34	8.879(4)
C7–C6' (d_6)	8.357(7)	8.29	7.534(5)
d_5- d_6	0.005(9)	0.06	1.345(6)

[a] The reported value 1.77 Å was corrected to be 1.75 Å by recalculation using the atomic coordinates reported in ref. 2.

In view of these findings, 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.

This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

REFERENCES AND NOTES

1. Preliminary report: J. Harada, K. Ogawa, and S. Tomoda, Chem. Lett., in press.
2. M. Ehrenberg, Acta Cryst., 20, 183 (1966).
3. E. Osawa and K. Kanematsu, in Molecular Structure and Energetics, edited by A. Greenberg and J. F. Liebman (Verlag Chemie International, Inc. Deerfield Beach, FL, 1986), Vol. 3, Chap. 7, pp. 329.
4. D. A. Dougherty, W. D. Hounshell, H. B. Schlegel, R. A. Bell, and K. Mislow, Tetrahedron Lett., 17, 3479 (1976).
5. D. A. Dougherty, C. S. Choi, G. Kaupp, A. B. Buda, J. M. Rudzinski, and E. Osawa, J. Chem. Soc., Perkin Trans. II, 1063 (1986).
6. X. Zhou, R. Liu, and N. L. Allinger, J. Am. Chem. Soc., 115, 7525 (1993).
7. T. R. Battersby, P. Gantzel, K. K. Baldridge, and J. S. Siegel, Tetrahedron Lett., 36, 845 (1995).
8. 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, $\beta = 111.968(9)°$, $V = 1019.3(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.331$ gcm^{-3}, Cu $K\alpha(\lambda = 1.54184$ Å), $\mu = 0.53$ 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.[2] The structure was refined by full-matrix least-squares method using XTAL system.[12] 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).
9. J. H. Golden, J. Chem. Soc., 3741 (1961).
10. 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, $\beta = 111.77(1)°$, $V = 997.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.36$ gcm^{-3}, $\mu = 0.54$ 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. $R(R_w) = 0.048(0.059)$.
11. A. Wada and J. Tanaka, Acta Cryst., B33, 355 (1977).
12. S. R. Hall, H. D. Flack, and J. M. Stewart, XTAL3.2. Universities of Western Australia, Geneva, and Maryland, (1992).