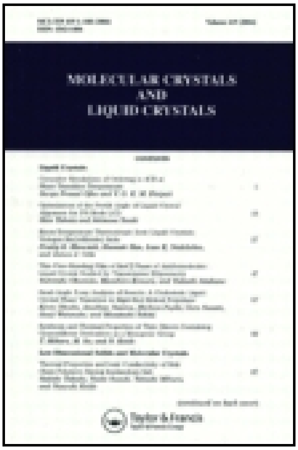

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Interpretation of Bond Length Anomaly: Molecular Motion and Reactions in Crystals

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Interpretation of Bond Length Anomaly: Molecular Motion and Reactions in Crystals

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Origins of the bond length anomalies observed for the X-ray structures of a series of organic compounds are discussed in terms of molecular motion and reactions in crystals.

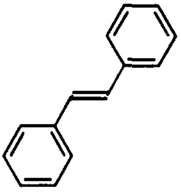
Keywords: X-ray crystallography; molecular crystals; bond length; molecular motion, crystalline state reactions

INTRODUCTION

The bond length obtained from X-ray crystallographic analysis, which is one of the most reliable experimental methods for the determination of molecular geometry, is sometimes anomalously short or long. The anomaly attracts much interests of chemists and is usually tried to be interpreted by chemically rational ways. However, the interpretation would be erroneous if dynamic aspects of molecular crystals is not taken into account. This paper shows the bond length anomalies observed in the X-ray structures of a series of organic compounds and discusses their origin in terms of molecular motion and reactions in crystals.

THE CENTRAL BOND LENGTH IN STILBENES

The ethylene bond length of (*E*)-stilbene (**1**) was determined to be in the range of 1.29 – 1.32 Å by X-ray diffraction at room temperature.[1] The results seem to be chemically unreasonable, because the ethylene bond, which is conjugated with the benzene rings, must be longer than the C=C bond of ethylene, of which length is known to be 1.337 Å.[2]



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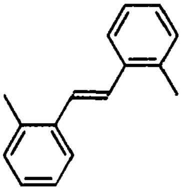

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A similar tendency was observed for other stilbenes. Most remarkable example is found in the X-ray structure of (*E*)-2,2'-dimethylstilbene (**2**).[3] The ethylene bond length was observed to be extremely short [1.283(3) Å] at 298 K. The bond length increases greatly with lowering the temperature. The length at 118 K [1.321(2) Å] is, however, still shorter than the length estimated from the molecular mechanics calculations [1.352 Å]. The bond angle θ and the torsion angle ω also show strong temperature dependence. With lowering the temperature, θ decreases [128.3(1) ° at 298 K and 126.4(1) ° at 118 K] and the absolute value of ω increases considerably [±11.7(3) ° at 298 K and ±18.0(2) ° at 118 K]. They approach the values estimated from the molecular mechanics calculations [θ = 124.1 ° and ω = ±27.3 °]. Other bond lengths and angles remain unchanged with variation of the temperature.

The results are rationalized by assuming the torsional vibration of the C–Ph bonds in crystals during which the movement of the benzene rings is restrained to be minimum, as shown in Figure 1.[4] The torsional vibration causes an interconversion between two conformations. The observed crystal structure would be an average of two conformations. The ethylene bond in the averaged structure is shorter than that in the true structure. The lower the temperature, the smaller the vibration amplitude. As a result, the observed length of the ethylene bond appears to become longer with the lowering the temperature. Temperature dependence of the torsion angle of the C–Ph bonds is explained in terms of the anharmonicity in the potential describing the torsional vibration of the C–Ph bonds.

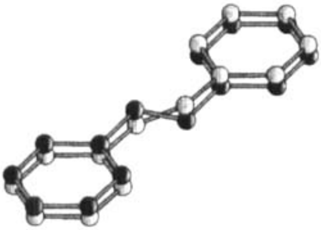
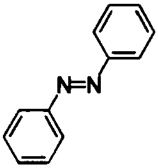


FIGURE 1 Torsional vibration in crystals

This phenomenon is found to widely occur in the crystals of stilbenes. The Cambridge Structural Database[5] search reveals that the observed length of the ethylene bond is always shorter than the theoretically expected length of 1.349 Å, which is obtained from the quantum mechanical calculations using the density functional method at B3LYP/6-31G* levels.[6]

A similar phenomenon was also observed for the crystals of azobenzenes[7] and *N*-benzylideneanilines.[8]

When the amplitude of the torsional vibration becomes much larger, a conformational interconversion between two conformers with different orientations can take place. For an example, one of two crystallographically independent molecules of azobenzene (3) performs the conformational interconversion between two conformers through the conformation in which



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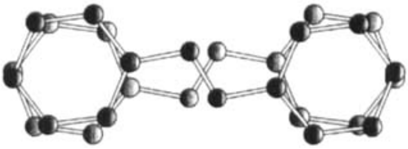
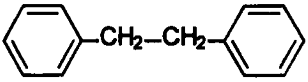


FIGURE 3 Orientational disorder of 3

the azo unit is perpendicular to the benzene rings. The conformational interconversion gives rise to an orientational disorder (Figure 3).

THE CENTRAL BOND LENGTH IN 1,2-DIPHENYLETHANE

The length of the central ethane bond in 1,2-diphenylethane (**4**) has been a subject of considerable interest for about half a century because of its remarkable shortening in the X-ray structures.[9] The length determined by X-ray diffraction (1.48 – 1.517 Å) was significantly shorter than the standard length of the $C(sp^3)$–$C(sp^3)$ bond [1.541(3) Å]. Redetermination of the X-ray structure at different temperatures shows that the ethane bond length substantially increases with lowering the temperature [1.506(5) Å at 240 K and 1.529(3) Å at 100 K].[10] The results can also be accounted for by assuming the torsional vibration of the C–Ph bonds during which the movement of the benzene rings is restrained to be minimum (Figure 2), although the shape of 1,2-diphenylethane is much different from that of stilbenes.



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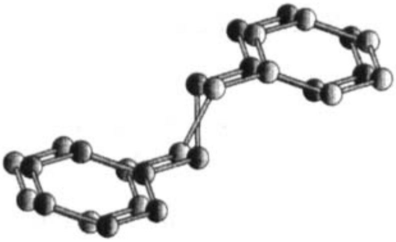
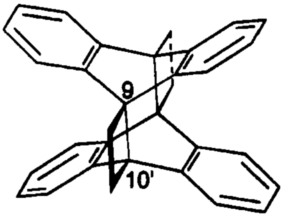


FIGURE 2 Torsional vibration in crystals

THE CENTRAL C–C BOND LENGTH IN THE BI(ANTHRACENE-9,10-DIMETHYLENE) PHOTOISOMER.

The central C–C bond (C9–C10’) of the photoisomer (**5**) of bi(anthracene-9,10-dimethylene) (**6**) has been known as one of the longest $C(sp^3)$-$C(sp^3)$ bonds. Its length was determined to be 1.77 Å by Ehrenberg using X-ray



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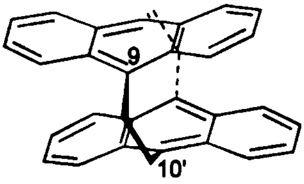

6

diffraction.[11] The anomalous bond elongation provoked great interest among organic and theoretical chemists, and several attempts to rationalize it have been made.[12]

Redetermination of the X-ray structure of **5** was carried out independently by Siegel *et al.*[13] and by us,[14] and it is established that the C9–C10' bond length is not 1.77 Å but 1.66 Å.

Then, why did the C–C bond appear to become extraordinarily long in the Ehrenberg's X-ray structure? It has been reported that compound **5** gradually changes into compound **6** in the solid state in the dark. 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 **5** changed into a single crystal of **6**.

The results suggest that isomer **6** could coexist in the crystal of **5** during the cycloreversion reaction. Coexistence of **6** would cause a disorder in the X-ray structure. If the population of **6** is much smaller than that of **5**, the disorder would be unresolvable. However, its effect would appear in the observed molecular geometry. If the crystal of **5** contains a small amount of **6**, the apparent length of C9–C10' would be substantially elongated, because the distance between C9 an C10' in **6** (2.77 Å) is much longer than that in **5** (1.66 Å).

Acknowledgments

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