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The Central Bond Length in 1,2-Diphenylethanes

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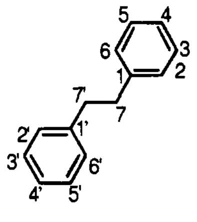
Abstract: Crystal structures of 1,2-diphenylethane (**1**) and 1,2-bis(2-methylphenyl)ethane (**3**) were determined at different temperatures by X-ray diffraction. The observed length of the central C−C bond in **1** at 240 K (1.506(5) Å) appears to be considerably shorter than the standard value of a $C(sp^3)-C(sp^3)$ bond (1.541(3) Å). The observed length, however, substantially increases with lowering of the temperature. On the contrary, the ethane bond length in **3** (1.534(5) Å and 240 K) is normal and remains constant at different temperatures. It is concluded that the anomaly in the ethane bond length of 1,2-diphenylethanes, which has been attempted to be explained in terms of various electronic effects, is an artifact caused by the torsional vibration of the C−Ph bonds in crystals.

The central bond length in 1,2-diphenylethane (**1**) has been a subject of considerable interest for more than half a century because of its remarkable shortening in the X-ray structures.[1−5] It might be expected to be elongated by the through-bond interaction of the σ orbitals of the ethane bond with the π orbitals of the benzene rings in the antiperiplanar conformation, in which this interaction can operate effectively because both phenyl rings are nearly perpendicular to the plane made by the three central C−C bonds.[6] The length determined by X-ray diffraction (1.48−1.517 Å),[2−4] however, was significantly shorter than the standard length of the $C(sp^3)-C(sp^3)$ bond (1.541(3) Å).[7] Jeffrey pointed out that the shortening is commonly observed for the central bond in a system in which two unsaturated groups are separated by three single bonds.[5,8] The phenomenon seems to be closely related to the ethane bond length problem of hexaphenylethanes, which has been a subject of much controversy.[9] Although considerable efforts were devoted to elucidation of the origin of the shortening, it still remains unclear. Winter and co-workers attributed the shortening to "a so far unrecognized electronic effect of the π-systems on the" ethane bond.[4] One of the difficulties of the problem is to give a rational explanation for the remarkable difference in the ethane bond length between **1** and a similar compound 1,2-bis(2-bromophenyl)ethane (**2**). The observed length of the ethane bond in **2** is almost normal (1.54(1) Å) in sharp contrast to that in **1**.[5,10] It seems to be difficult to explain the phenomenon by any electronic effect.



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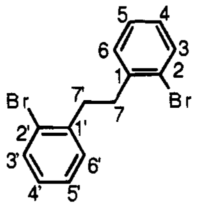

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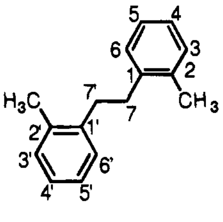

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We wish to report here an answer for the long-standing problem based on the X-ray crystal analyses of **1** and a model compound of **2**, 1,2-bis(2-methylphenyl)ethane (**3**), at different temperatures.[11]

Experimental Section

Materials. Compounds **1** and **3** were purchased from Tokyo Kasei Co. and Aldrich Co., respectively. Single crystals of **1** and **3** for the X-ray diffraction were obtained by slow evaporation of the hexane and the methanol solution at room temperature, respectively.

X-ray Crystallography. All diffraction measurements were made on a Rigaku AFC-6A diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.541 84 Å). An Oxford Cryostream cooler was used for the low-temperature measurements. The integrated intensities were collected in the $2\theta-\omega$ scan mode with an ω rate of 8.0 deg min^{-1}. The intensities were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct method and refined by full-matrix least-squares method using the XTAL system.[12] All the hydrogen atoms were located from difference maps and refined isotropically. All the carbon atoms were refined anisotropically. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. Calculations of geometrical parameters and drawings of ORTEP diagrams were performed by XTAL system. Full details for the crystallographic analysis are described in the supplementary material.

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[10] Corey, E. R. *Acta Crystallogr.* **1979**, *B35*, 201−203. Corey reported a remarkable shortening for the central bond (1.49(2) Å) at room temperature. Kahr redetermined the structure with substantially higher accuracy and obtained an almost normal length (1.54(1) Å) for the central bond (ref 5).

[11] Compound **2** itself is not suitable for accurate determination of the position of carbon atoms because of the too large X-ray scattering factor of bromine atoms.

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Table 1. Selected Geometrical Parameters for **1** and **3**[a]

compd	origin	temp (K)	dist (Å), d_0	dist (Å), d_1	bond angle (deg), θ	torsion angle (deg), ω
1	X-ray	240	1.506(5)	1.508(4)	113.9(3)	±72.0(4)
		180	1.522(3)	1.510(3)	113.4(2)	±69.5(3)
		100	1.529(3)	1.513(3)	113.2(2)	±65.3(2)
	MM3(92)		1.538	1.511	111.7	±90.3
3	X-ray	240	1.534(5)	1.515(5)	112.1(3)	±86.4(5)
		90	1.541(3)	1.512(3)	112.4(2)	±86.5(3)
	MM3(92)		1.539	1.513	111.8	±86.4

[a] Definitions of the geometrical parameters are as follows: d_0, C7−C7′; d_1, C1−C7, C1′−C7′; θ, C7′−C7−C1, C7−C7′−C1′; ω, C6−C1−C7−C7′, C6′−C1′−C7′−C7.

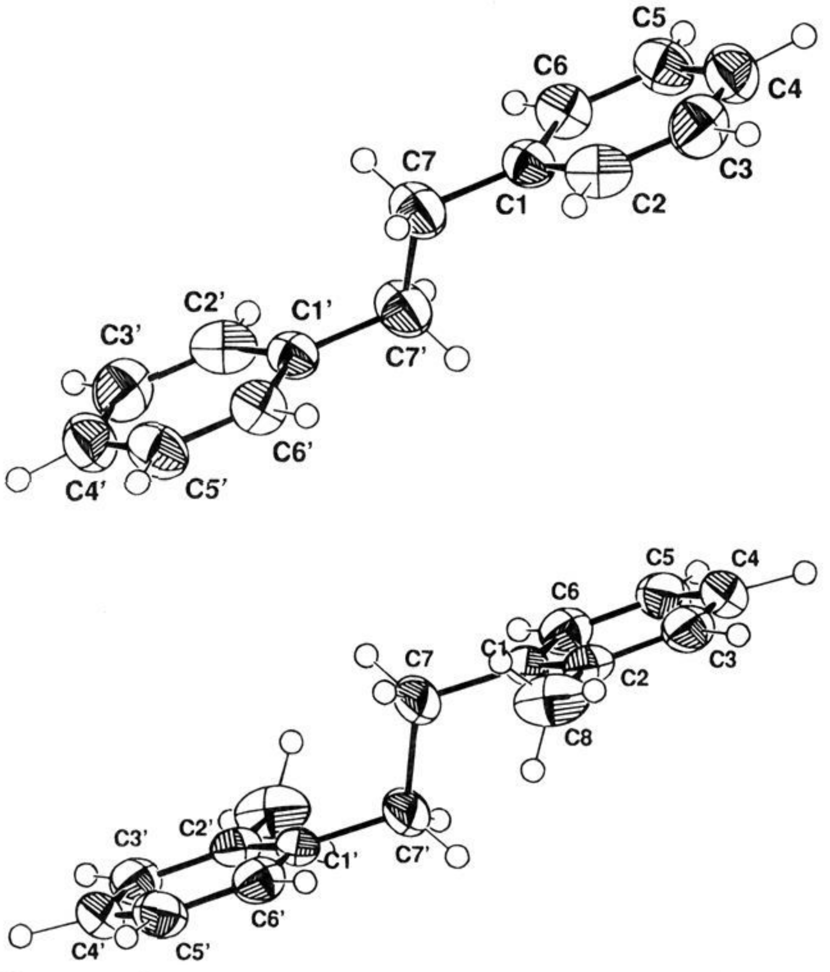

Figure 1. ORTEP drawings. The thermal ellipsoids of the carbon atoms are scaled to the 50% probability level; the hydrogen atoms are shown as spheres of a fixed, arbitrary size. (top) **1** at 240 K. (bottom) **3** at 240 K.

Crystallographic Data for 1: $C_{14}H_{14}$, MW = 182.27, monoclinic, space group $P2_1/n$, $Z = 2$. At 240 K: $a = 7.6203(8)$, $b = 6.186(1)$, and $c = 11.645(1)$ Å, $\beta = 100.336(8)°$, $V = 540.1(1)$ Å^3, R (R_w) = 0.053 (0.059). At 180 K: $a = 7.526(1)$, $b = 6.185(2)$, and $c = 11.631(1)$ Å, $\beta = 100.66(1)°$, $V = 532.0(2)$ Å^3, R (R_w) = 0.044 (0.049). At 100 K: $a = 7.424(2)$, $b = 6.158(1)$, and $c = 11.637(1)$ Å, $\beta = 101.36(1)°$, $V = 521.5(2)$ Å^3, R (R_w) = 0.042 (0.048).

Crystallographic Data for 3: $C_{16}H_{18}$, MW = 210.32, orthorhombic, space group $Pbca$, $Z = 4$. At 240 K: $a = 12.829(1)$, $b = 6.9962(7)$, and $c = 14.018(1)$ Å, $V = 1258.2(2)$ Å^3, R (R_w) = 0.062 (0.073). At 90 K: $a = 12.784(1)$, $b = 6.9592(7)$, and $c = 13.790(1)$ Å, $V = 1226.9(2)$ Å^3, R (R_w) = 0.048 (0.059).

Results and Discussion

Single crystal X-ray diffraction measurements were carried out for **1** at 240, 180, and 100 K and for **3** at 240 and 90 K. The selected geometrical parameters are listed in Table 1, and the ORTEP diagrams are shown in Figure 1.

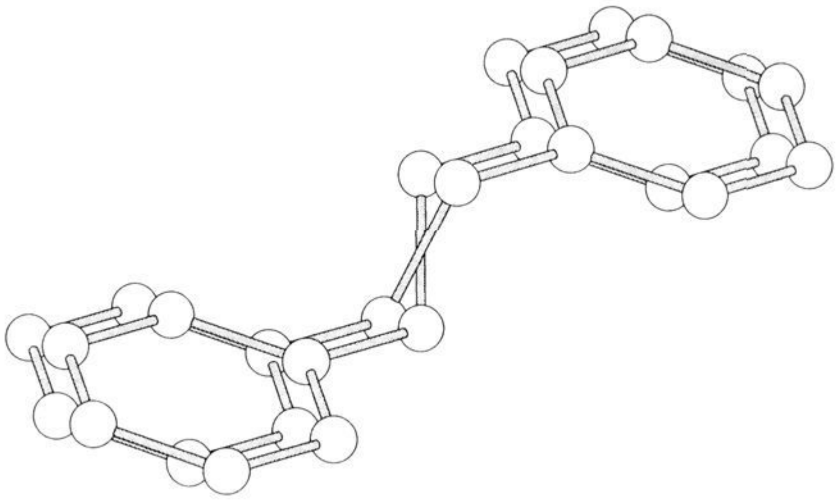

Figure 2. Vibration model for **1**, drawn by the program MindTool.[16]

The molecular structure of **1** observed at 240 K is essentially identical with that so far reported. The molecule lies at the crystallographic inversion center. The two phenyl rings are parallel to each other. The dihedral angles between the phenyl rings and the plane made by C1, C7, C7′, and C1′ are nearly right angles, as shown by the torsion angles in Table 1. The length of the ethane bond C7−C7′ (1.506(5) Å at 240 K) is considerably shorter than the value predicted by the MM3 calculations[13] (1.538 Å) and substantially increases with lowering of the temperature. The length at 100 K is significantly longer than that at 240 K, but still shorter than the MM3 value. The torsion angles strongly depend on the temperature. The absolute values of the angles decrease with lowering of the temperature. Other geometrical parameters are almost unchanged with variation of the temperature.

An apparent shrink of interatomic distance has usually been interpreted by libration of the molecule regarded as a rigid body (the rigid body model).[14] The results for **1**, however, cannot be explained by the rigid body model because the temperature dependence of the observed geometry appears only in the central part of the molecule. A similar phenomenon was observed for (*E*)-stilbenes and successfully explained in terms of intramolecular motion in crystals.[15] The results for **1** can also be explained by assuming the vibration in the direction nearly perpendicular to the plane made by the central four carbon atoms C1, C7, C7′, and C1′, as shown in Figure 2.

According to this model, the observed molecular structure is an average of the two conformers that are interconverted by the torsional vibration of the C−Ph bonds during which the movement of the benzene rings is restrained to be minimum. The ethane bond length 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 ethane bond appears to become longer with lowering of the temperature. The temperature dependence of the torsion angles is attributed to the anharmonicity in the potential describing the torsional vibration of the C−Ph bonds in crystals.

This interpretation is substantiated by the calculations in which the observed molecular structure is assumed to be an average of a 1:1 mixture of the two conformers in the above model (Table 2). Molecular structures of all of the conformers were refined by MM3 calculations except for the torsion angles of the C−Ph bonds (ω's). The ethane bond of all of the MM3 structures has nearly the same length (1.538−1.539 Å). The calculations well reproduced all of the X-ray structures and their temperature dependences: the average structure of the two conformers with ω's of ±60° and ±85° is almost identical with

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Table 2. Molecular Structure Calculated from the Vibration Model[a]

structure	d_0 (Å)	d_1 (Å)	θ (deg)	ω (deg)
A	1.538	1.511	112.1	±85.0
B	1.538	1.511	112.1	±80.0
C	1.539	1.511	112.3	±70.0
D	1.539	1.511	113.2	±60.0
(A + D)/2[b]	1.510	1.511	113.1	±72.6
(B + D)/2[c]	1.520	1.512	112.9	±70.1
(C + D)/2[d]	1.534	1.512	112.8	±65.1

[a] Definitions of the geometrical parameters are given in the legend of Table 1. [b] Average of a 1:1 mixture of structures A and D. [c] Average of a 1:1 mixture of structures B and D. [d] Average of a 1:1 mixture of structures C and D.

the X-ray structure at 240 K (d_0 = 1.506(5) Å, ω = ±72.0(4)°); the average structure of the two conformers with ω's of ±60° and ±80° and that with ω's ±60° and ±70° also reproduce the X-ray structure at 180 K (d_o = 1.522(3) Å, ω = ±69.5(3)°) and that at 100 K (d_0 = 1.529(3) Å, ω = ±65.3(2)°), respectively.

The observed molecular structure of **3** is essentially identical with that of **1**. The molecule lies at the crystallographic inversion center. The two phenyl rings are parallel to each other. The absolute values of the torsion angels C6−C1−C7−C7′ and C6′−C1′−C7′−C7 are almost 90°. The ethane bond length is, however, normal (1.534(5) Å at 240 K) and remains constant with lowering of the temperature. The molecular structure does not depend on the temperature and agrees fairly well with that predicted by MM3 calculations. The results make a sharp contrast with those of **1** and are almost the same as those of **2**.

The difference in the observed molecular structures between **1** and **3** is ascribed to the difference in the amplitude of the torsional vibration. The amplitude in **3** as well as **2** is expected to be much smaller than that in **1** because the torsional potential in the former must be steeper than that in the latter due to the steric congestion caused by the methyl or the bromo group on the ortho position of the benzene ring. As a result, the apparent shortening of the ethane bond and the temperature dependence of the observed molecular structure become negligibly small.

It is therefore concluded that the unusually short ethane bond of 1,2-diphenylethanes in the X-ray structures is an artifact caused by the torsional vibration of the C−Ph bonds in crystals. The true length of the ethane bond is safely estimated to be 1.54 Å. Thus, it is not necessary to consider an electronic effect to explain the anomaly in the ethane bond length of 1,2-diphenylethanes.

Acknowledgment. We thank Professor Bart Kahr of Purdue University for sending us his dissertation, which gives an excellent review of the subject.

Supplementary Material Available: Listings of the crystallographic information files (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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