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The Central Bond Length in 1,2-Diarylethanes

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Abstract: The structures of several vicinal diarylethanes are determined by X-ray crystallography and calculated by Hartree−Fock *ab initio* computations. The structure of the general class of 1,2-diarylethanes is discussed, and a "standard molecular fragment" is derived from a search of the Cambridge Structural Database. The anomalously short $C_{sp^3}-C_{sp^3}$ (central) bond reported for the parent 1,2-diphenylethane and some derivatives is not representative of the average molecular geometry derived from the database and is likely an experimental artifact. High-level split valence *ab initio* calculations predict a normal (1.54 Å) bond length for C_{2h} 1,2-diphenylethane.

Structural studies of molecules with two aryl rings separated by three σ bonds have produced claims of either anomalously long or short central bonds due to electronic effects between σ and π subsystems.[3] These claims are based specifically on crystallographic measurements of the central bond lengths in vicinal substituted polyarylethanes. However, the accuracy of some of these structure determinations has been questioned.[4] In the case of 1,2-diarylethanes, a wide range of central bond lengths have been reported. The possibility that the crystal structures of 1,2-diarylethanes are particularly beset with artifacts led us to reconsider the existing set of structures, add new structures with the intention of amplifying special electronic effects should they exist, and compute a series of high-level *ab initio* based geometries to serve as a reference.

Results and Discussion

One way to establish a "standard molecular fragment" for a common group of connected atoms is to sample a significant population of existing structures. A survey of the Cambridge Structural Database (CSD) reveals over one dozen compounds with structural fragments that can be viewed as unconstrained simple 1,2-diarylethanes.[5,6] These structure determinations vary in quality, with several having R factors greater than 0.10 and estimated standard deviations on the order of picometers. In addition, several compounds have been multiply determined with as much as 10 picometers (0.1 Å) difference between the high and low value of the central bond length. Clearly, the

crystallographic results for this class of compounds have been inconsistent. Nonetheless, all the structures in this class have a bulk (unfiltered) average central bond length of 1.526(6) Å: structures with $R < 0.08$ give a mean value of 1.534(6) Å. Both the filtered and bulk values are well within statistical variance of the mean bond length for $C\#-CH_2-CH_2-C\#$ compounds in general ($X = 1.524(14)$), as derived from the CSD.[7]

The average value for the $C_{sp^2}-C_{sp^3}$ bonds flanking the central bond in the 1,2-diarylethane structures is 1.511(6) Å, with a filtered average of 1.513(5) Å. These values also fall well within the normal range when compared to the CSD value of 1.510(9) Å for $C\#-CH_2-C_{Ar}$ bonds.[7] Therefore, unusual electronic effects are not evident from the "standard molecular fragment."

If electronic effects were structurally significant, they should lead to different geometries in molecules bearing strong electron donating or withdrawing groups; comparable geometries would imply that electronic effects are at best weak. The structures 1,2-bis(2-methoxyphenyl)ethane,[5s] 1,2-bis(4-methylphenyl)-

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(3) Two rationales for these bond length distortions are commonly articulated: (1) The aryl rings conjugate through the intervening σ bond, through-bond coupling (Hoffman, R. *Acc. Chem. Res.* **1971**, *4*, 1−9. Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696−701); (2) The aryl rings induce a rehybridization of the α carbon. In the first scenario, the $C_{sp^3}-C_{sp^3}$ (central) bond should lengthen and the $C_{sp^3}-C_{sp^2}$ (flanking) bond should shorten; the bond angle $C_{sp^3}-C_{sp^3}-C_{sp^2}$ should be smaller than the standard value. The consequences of rehybridization can be varied; the central bond may lengthen or shorten depending upon the angle deformations. Caution is of course necessary when rationalizing metric anomalies with simple fragment orbital interactions. See: Osawa, E.; Kanematsu, K. In *Molecular Structure and Energetics*; Greenberg, A., Liebman, J. F., Eds.; VCH: Deerfield Beach, FL, 1986; Chapter 7.

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Scheme 1

Figure 1. ORTEP representations for **1–4**.
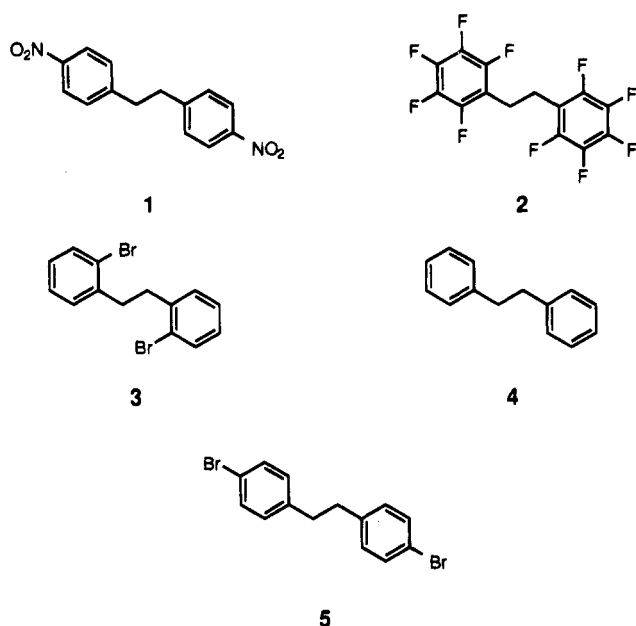
ethane,[5e] and 1,2-bis(2,4,6-trimethylphenyl)ethane[5p] exemplify systems containing electron donating methoxy and methyl groups. The average bond lengths for these compounds are 1.54 Å (central) and 1.51 Å (flanking). Because of the lack of structures with electron withdrawing groups, we determined the X-ray structures of 1,2-bis(4-nitrophenyl)ethane (**1**) and 1,2-bis(2,3,4,5,6-pentafluorophenyl)ethane (**2**). ORTEP representations of these and related molecules are shown in Figure 1. The relevant bond lengths in **1** and **2** are 1.536(4) and 1.526(5) Å (central) and 1.512(3) and 1.503(3) Å (flanking), respectively. Given the precision of these analyses, it is unlikely that previous metric anomalies in 1,2-diarylethanes are due to systematic electronic (i.e., simple orbital) effects.

The most egregious case of a short central bond (1.49(2) Å) was reported for 1,2-bis(2-bromophenyl)ethane (**3**).[5h] The initial structure determination was based on 480 reflections; we redetermined the structure from 729 reflections. After anisotropic refinement, we found that the central bond in **3** was equal to 1.54(1) Å, which is in marked contrast to the short central bond previously reported.

One other structure which remains an outlier, despite multiple redeterminations, is the parent diphenylethane (**4**). The first X-ray examination produced the cell constants and space group ($P2_1/a$).[8] Robertson's 1934 analysis, based on 150 photometrically measured reflections, showed that **4**, unlike the aromatic compounds that had been studied in detail previously, exhibited a three-dimensional rather than a planar structure.[9] The phenyl rings, while themselves planar, were found to occupy parallel planes that were at approximate right angles to the connecting σ skeleton. A Fourier synthesis published the next year gave values of 1.58 and 1.47 Å for the central and flanking lengths, respectively. The central bond distance was overestimated because the hydrogen atoms were not included in the calculated structure factors.[5a] Jeffrey redetermined the structure of **4** using 746 intensities and found a substantially shortened central bond of 1.48 Å and a flanking bond of 1.50 Å.[10] From the intensity consistency of the molecular geometry, he judged the figures to be reliable to ±0.01 Å. Jeffrey proposed that
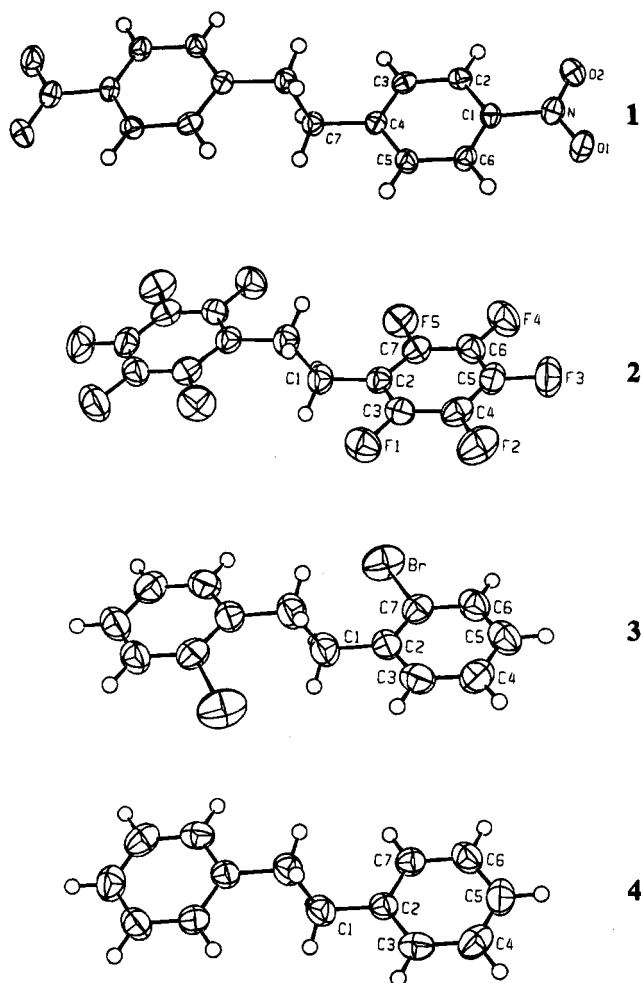
this shortening was a general characteristic of the central bond in a system in which two unsaturated groups are separated by three single bonds.[11]

Cruickshank reevaluated Jeffrey's structure of **4** in 1949 and applied corrections for computational errors and effects from termination of the Fourier series at a finite *hkl* value.[5c] He reported 1.51(1) and 1.52(1) Å as the corrected lengths for the central and flanking bonds, respectively. The central bond length, while larger than Jeffrey's value, remained short. Winter, Butters, and Rieker redetermined the structure of **4** in 1982. Although the details of this structure were not published, they remarked in a related paper that "High-angle refinement with low-temperature data leads to 1.517(3) Å for the central bond" in 1,2-diphenylethane.[5d] This result supports Jeffrey's claim of a short central bond length for **4**.

Given the historical importance of **4** and our findings for **3**, we also redetermined the structure of **4** using 1042 reflections (Mo Kα, 2Θ ≤ 60°, at 218 K). To our surprise, the central bond length (1.502(4) Å) was not only short compared to the standard value but was comparable to the flanking bond length (1.509(2) Å). This indicates that **4** either has an anomalously short central bond length as compared to the "standard molecular fragment" or there is a substantial experimental artifact.

A short central (C=C) bond has also been observed in (*E*)-stilbene.[12] Ogawa's meticulous analysis of the room temperature structure showed that the shortening was due to librational motions of the molecules in the crystal; at 113 K a normal C=C bond length was found.[13] Such motions are well-known causes

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Table 1. Select Experimental and Computational Geometries for **1–7**

	experiment (X-ray)				computation (6-31G(D))[a]		
Compd	central (Å)	flanking (Å)	angle[b] (deg)	torsion[c] (deg)	central (Å)	flanking (Å)	angle[b] (deg)
1	1.536(4)	1.512(3)	111.3(2)	77.6(2), 80.4(2)	1.543	1.513	112.2
2	1.526(5)	1.503(3)	111.9(2)	80.8(2), 84.1(2)	1.540	1.512	112.0
3	1.54(1)	1.497(7)	112.0(5)	89.2(5), 89.8(5)	1.542	1.515	112.3
4	1.502(4)	1.509(2)	113.7(2)	82.9(2), 82.8(2)	1.542	1.514	112.7
5					1.542	1.513	112.5
6					1.530	1.5307	113.4
7					1.532	1.537	114.9
X[d]	1.534	1.513					

[a] Optimized in C_{2h} symmetry. The 6-31G(D) basis set used in the calculations incorporates the Binning–Curtiss double-ζ basis set (14s, 11p, 5d)/[6s, 4p, 1d] for bromine.[22] [b] C_{sp^3}–C_{sp^3}–C_{sp^2}. [c] C_{sp^3}–C_{sp^3}–C_{ipso}–C_{ortho}. [d] Average over 1,2-diphenylethane crystal structures with $R < 0.08$.

of artifactual bond shortening, and it is likely that they are responsible for the apparent shortening of the central bond in **4**.[14] In fact, librational shortening of the central bond in **4** is illustrated in the accompanying paper by Harada, Ogawa, and Tomoda.[15]

Given a sufficient basis set, Hartree–Fock *ab initio* computations should provide an excellent reference for the ground state molecular geometries of vicinal diarylethanes.[16] There is good precedence that HF/6-31G(D) is adequate for hydrocarbon and first row derivatives of **4**. In the calculation of **3** and **5** (1,2-bis(4-bromophenyl)ethane), bromine is treated with the Binning–Curtiss double-ζ basis set (14s, 11p, 5d)/[6s, 4p, 1d][17] augmented with polarization functions. All other elements in these two molecules are treated with the 6-31G(D) basis set. Given the excellent agreement of the experimental and computational geometries, we judge this level of theory appropriate for the present study.

The C_{2h} calculated structures of **1–5** show remarkably similar core geometries: the central bond lengths are 1.543, 1.540, 1.542, 1.542, and 1.542 Å; the flanking bond lengths are 1.513, 1.512, 1.515, 1.514, and 1.513 Å; the bond angles (C_{sp^3}–C_{sp^3}–C_{sp^2}) are 112.2°, 112.0°, 112.3°, 112.7°, and 112.5°. The computational geometries are compared with the experimental X-ray geometries in Table 1.

The core geometries for **1–5** match the standard molecular fragment; they are not significantly altered by phenyl ring substitution. Furthermore, the central bonds in hexane (**6**, 1.530 Å) and 1,2-dicyclohexylethane (**7**, 1.532 Å), calculated at the 6-31G(D) level, are at worst slightly shorter than the central bonds in **1–5**. Thus, these computational reference structures also indicate that 1,2-diarylethanes ought not show any geometric anomalies and that these ordinary structures can be understood without invoking any novel electronic interactions.

In conclusion, we suggest restraint in the interpretation of molecular geometries obtained from room temperature X-ray structures. Even simple systems sometimes hide artifacts behind

unblemished atomic displacement parameters and ordinary refinement indicators.

Experimental Section

General Methods. Compound **4** was purchased (Aldrich) and recrystallized from ethanol before use. Compounds **1–3** were synthesized by literature methods.[18]

Crystallography of 1,2-Bis(4-nitrophenyl)ethane (1). Single crystals of **1** were grown from benzene. A red crystal with dimensions 0.18 × 0.28 × 0.39 mm³ was mounted and centered on a Siemens R3m diffractometer. Crystal data: $C_{14}H_{12}N_2O_4$; monoclinic (space group $P2_1/c$); $a = 4.487(2)$ Å, $b = 13.281(6)$ Å, $c = 10.756(5)$ Å, $\beta = 98.24(3)°$; $V = 634.3(5)$ Å³, $d_{calcd} = 1.426$ g·cm⁻³, $\mu = 0.99$ cm⁻¹, $Z = 2$. X-ray intensities were recorded at 173 K by applying Mo Kα radiation ($\lambda = 0.710\,73$ Å) and Wycoff scans from 3° < 2Θ < 60°. A total of 1854 independent reflections were collected of which 1045 were considered observed ($|F_o| > 6.0\sigma|F_o|$). The structure was solved by direct methods with a PC version of Siemens SHELXTL PLUS. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods; hydrogens were located in successive difference maps and refined with a riding model. The R and R_w factors after refinement of 94 parameters were 0.047 and 0.065, respectively. The largest peak in the final Fourier difference map was 0.28 e·Å⁻³.

Crystallography of 1,2-Bis(2,3,4,5,6-pentafluoro)ethane (2). Single crystals of **2** were grown from ethanol. A crystal measuring 0.30 × 0.15 × 0.11 mm³ was mounted and centered on an Enraf-Nonius CAD4 diffractometer. Crystal data: $C_{14}H_4F_{10}$; monoclinic (space group $P2_1/n$); $a = 8.931(4)$ Å, $b = 5.826(4)$ Å, $c = 12.489(6)$ Å, $\beta = 90.2(2)°$; $V = 649.8(1)$ Å³, $d_{calcd} = 1.851$ g·cm⁻³, $\mu = 2.01$ cm⁻¹, $Z = 2$. X-ray intensities were recorded at 293 K by applying Mo Kα radiation ($\lambda = 0.710\,73$ Å) and $\omega-2\Theta$ scans from 5° < 2Θ < 50°. A total of 1147 independent reflections were collected of which 639 were considered observed ($|F_o| > 3.0\sigma|F_o|$). The structure was solved by direct methods with SHELX-86 as provided in the MolEN package of programs. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods; hydrogens were located, and their positions and isotropic thermal parameters were refined. The R and R_w factors after refinement of 109 parameters were 0.031 and 0.041, respectively. The largest peak in the final Fourier difference map was 0.11 e·Å⁻³.

Crystallography of 1,2-Bis(2-bromophenyl)ethane (3). Single crystals of **3** were grown from ethanol/hexane by slow evaporation. A crystal of 0.12 × 0.23 × 0.25 mm was mounted on a glass fiber and centered on a Nicolet R3m four-circle diffractometer. Crystal data: $C_{14}H_{12}Br_2$; orthorhombic (space group $Pbca$); $a = 14.660(3)$ Å, $b = 13.252(4)$ Å, and $c = 6.673(2)$ Å; $V = 1296.4(5)$ Å³, $d_{calcd} = 1.742$ g·cm⁻³, $\mu = 85.4$ cm⁻¹, $Z = 4$. X-ray intensities were recorded at 293 K by applying Cu Kα radiation ($\lambda = 1.541\,78$ Å) and ω scans from 3° < 2Θ < 114°. A total of 990 independent reflections were collected of which 729 were considered observed ($|F_o| > 3\sigma|F_o|$). Empirical absorption corrections were applied on the basis of azimuthal scans of 11 suitable reflections; the maximum and minimum transmissions were 0.786 and 0.248, respectively. R_m values before and after the correction

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were 0.157 and 0.063, respectively. The structure was refined starting from Corey's parameters.[5h] All non-hydrogen atoms were refined anisotropically. The phenyl hydrogens were included at ideal positions (C—H = 0.96 Å, C—C—H = 109.5° and 120.0°) and varied using a riding model. The R and R_w factors after refinement of 73 parameters were 0.045 and 0.050, respectively. The largest peak in the final Fourier difference map was 0.46 e·Å^{-3}.

Crystallography of 1,2-Diphenylethane (4). Single crystals of **4** were grown from ethanol. A crystal measuring $0.12 \times 0.23 \times 0.25$ mm^3 was mounted on a glass fiber and centered on the diffractometer. Crystal data: C$_{14}$H$_{14}$; monoclinic (space group $P2_1/c$); $a = 7.635(2)$ Å, $b = 6.178(2)$ Å, $c = 12.720(3)$ Å, and $\beta = 115.86(2)°$; $V = 540.2$-(2) Å^3, $d_{calcd} = 1.12$ g·cm^{-3}, $\mu = 0.70$ cm^{-1}, $Z = 2$. X-ray intensities were recorded at 218 ± 3 K on a Nicolet R3m four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and an ω scan technique, $3° \leq 2\Theta \leq 60°$. A total of 1780 independent reflections were collected of which 1042 were considered observed ($|F_o| > 3\sigma|F_o|$). Empirical absorption corrections were applied on the basis of azimuthal scans of 12 suitable reflections; the maximum and minimum transmissions were 0.991 and 0.829, respectively. R_m values before and after the corection were 0.023 and 0.017, respectively. The structure was solved by direct methods although previous solutions had been reported.[9,10b,11] All non-hydrogen atoms were refined anisotropically. The ethane and phenyl hydrogens were included at ideal positions (C—H = 0.96 Å, C—C—H = 109.5° and 120.0°) and varied using a riding model. The R and R_w factors after refinement of 64 parameters were 0.071 and 0.066, respectively. The largest peak in the final Fourier difference map was 0.22 e·Å^{-3}.

Computational Methods. Geometries at all stationary points have been determined with *ab initio* methods, at the restricted Hartree—Fock (RHF) self-consistent field (SCF) level of theory. The *ab initio* calculations were performed using the 6-31G(D)[19,20] basis set that includes six *d* polarization functions on all heavy atoms and incorporates the Binning—Curtiss double-ζ basis set (14s, 11p, 5d)/[6s, 4p, 1d] for bromine.[19] Geometry optimizations were performed with the aid of the determined gradients and the search algorithms contained in GAMESS.[21] The nature of each SCF stationary point was established by calculating analytically and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies.

Supplementary Material Available: Tables giving data collection and refinement parameters, positional parameters, atomic displacement parameters, bond lengths, and valence angles for **1, 2, 3,** and **4** (17 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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