Registry No. $CuBr_2$·Tempo, 113132-33-5; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7.

Supplementary Material Available: Listing of atomic positional parameters (1 page). Ordering information is given on any current masthead page.

The Electronic Structures of *trans*- and *cis*-Bicyclo[4.1.0]hept-3-ene. Evidence for a Twist, Bent σ Bond

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trans-Bicyclo[4.1.0]hept-3-ene (**1**) has been synthesized recently,[1] and its isomerization to its cis isomer **2**[2] has been studied.[3] Hydrocarbon **1** is of interest because of the possible presence of a twist, bent σ bond between the bridgehead carbons C_1 and C_6.[4]

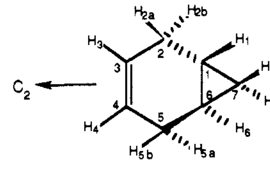
TOP VIEW

EDGE VIEW

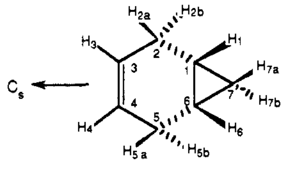
Although two decades have passed since the existence of this novel type of carbon–carbon bonding was first proposed,[4] unequivocal evidence for the presence of a twist-bent carbon–carbon σ bond has not been presented.[3] Herein, we present the results of our theoretical calculations on whether such novel bonding exists in **1** or **2**.

The ab initio calculations were done by using the program GRADSCF[5] on a CRAY-1A computer. Initial geometries were constructed by using CHEMX[6] and partially optimized. Subsequently, the geometries were symmetrized, **1** (C_2) and **2** (C_s), and gradient[7] optimized at the SCF level with the STO-3G basis set.[8] The final gradient optimizations were done with a double-ζ basis set augmented by d functions on carbon giving a basis set of the form (9s5p1d/4s)/[3s2p1d/2s].[9,10] At the optimimum SCF geometry, the force field was determined analytically[11] together with a correction for correlation effects at the MP2 level.[12]

Table I. Optimized Structural Parameters for **1** and **2**



1



2

	Bond Distances (Å)		
$r(C_1–C_7)$	1.509	$r(C_1–C_7)$	1.503
$r(C_1–C_6)$	1.491	$r(C_1–C_6)$	1.506
$r(C_1–C_2)$	1.511	$r(C_1–C_2)$	1.519
$r(C_2–C_3)$	1.541	$r(C_2–C_3)$	1.508
$r(C_3–C_4)$	1.340	$r(C_3–C_4)$	1.325
$r(C_1–H_1)$	1.080	$r(C_1–H_1)$	1.077
$r(C_2–H_{2a})$	1.087	$r(C_2–H_{2a})$	1.087
$r(C_2–H_{2b})$	1.086	$r(C_2–H_{2b})$	1.087
$r(C_3–H_3)$	1.078	$r(C_3–H_3)$	1.078
$r(C_7–H_7)$	1.077	$r(C_7–H_{7a})$	1.078
		$r(C_7–C_{7b})$	1.077
	Bond Angles (deg)		
$\theta(C_1–C_7–C_6)$	59.2	$\theta(C_1–C_7–C_6)$	60.1
$\theta(C_1–C_7–H_{7a})$	115.1	$\theta(C_1–C_7–H_{7a})$	117.5
$\theta(C_1–C_7–H_{7b})$	121.9	$\theta(C_1–C_7–H_{7b})$	118.3
$\theta(H_{7a}–C_7–H_{7b})$	113.6	$\theta(H_{7a}–C_7–H_{7b})$	114.6
$\theta(C_6–C_1–C_7)$	60.4	$\theta(C_6–C_1–C_7)$	59.9
$\theta(C_2–C_1–C_7)$	141.3	$\theta(C_2–C_1–C_7)$	120.0
$\theta(C_2–C_1–C_6)$	109.4	$\theta(C_2–C_1–C_6)$	120.6
$\theta(C_7–C_1–H_1)$	109.0	$\theta(C_7–C_1–H_1)$	115.7
$\theta(C_6–C_1–H_1)$	111.1	$\theta(C_6–C_1–H_1)$	116.0
$\theta(C_2–C_1–H_1)$	109.3	$\theta(C_2–C_1–H_1)$	114.1
$\theta(C_1–C_2–C_3)$	102.2	$\theta(C_1–C_2–C_3)$	113.9
$\theta(C_1–C_2–H_{2a})$	113.9	$\theta(C_1–C_2–H_{2a})$	109.3
$\theta(C_1–C_2–H_{2b})$	113.3	$\theta(C_1–C_2–H_{2b})$	109.8
$\theta(C_3–C_2–H_{2a})$	109.8	$\theta(C_3–C_2–H_{2a})$	108.3
$\theta(C_3–C_2–H_{2b})$	110.6	$\theta(C_3–C_2–H_{2b})$	109.1
$\theta(H_{2a}–C_2–H_{2b})$	107.1	$\theta(H_{2a}–C_2–H_{2b})$	106.1
$\theta(C_2–C_3–C_4)$	125.3	$\theta(C_2–C_3–C_4)$	125.0
$\theta(C_2–C_3–H_3)$	116.7	$\theta(C_2–C_3–H_3)$	116.2
$\theta(C_3–C_4–H_4)$	117.9	$\theta(C_3–C_4–H_4)$	118.8

The optimized geometries are given in Table I. The cis isomer **2** should not have significantly more strain than that associated with cyclopropane, and the structural parameters should be those for normal hydrocarbons. In support of this premise, the C–C bonds in the cyclopropane moiety of **2** are essentially the same as those found for cyclopropane with this basis set.[13] The only change is in $\theta(C_2C_1C_7)$ which is increased by 2°. The double bond of **2** also has the expected geometry parameters.[10] Overall the only significant differences from a "normal" bonding parameter for **2** occurred at C_2 where $\theta(C_1C_2C_3)$ increased by 4.4° from the tetrahedral value and $\theta(H_{2a}C_2H_{2b})$ was 3.4° smaller than tetrahedral.

Our calculations for the trans isomer **1** show significant deviations in the bond angle parameters relative to **2**. In comparison, only modest changes are found for the bond lengths. For example, $r(C_3{=}C_4)$ increased by 0.015 Å and $r(C_2–C_3)$ increased by 0.033 Å in **1** relative to **2**. This change in $r(C_2–C_3)$ gave a bond length significantly longer than a normal $sp^2–sp^3$ bond. The bond lengths

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(5) GRADSCF is an ab initio gradient program system designed and written by A. Komornicki at Polyatomics Research.

(6) CHEMX (Molecular Modeling System) is a program developed and distributed by Chemical Design, Oxford, England.

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(13) The parameters for cyclopropane are the following: $r(C–C) = 1.504$ Å, $r(C–H) = 1.076$ Å, $\theta(HCH) = 114.6°$, $\theta(CCH) = 117.9°$.

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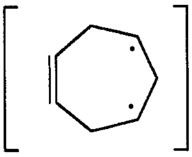
$r(C_1-C_6)$ and $r(C_1-C_2)$ of **1** were 0.015 and 0.008 Å less, respectively, than the corresponding bond lengths in **2**. As indicated above, major changes in bond angles occurred in **1** relative to **2**. For example, $\theta(C_2C_1C_7)$ increased by 21° in **1** to a value of 141.3°. As a consequence, the three exterior angles $\theta(H_1C_1C_x)$ in **1** all show a decrease relative to the corresponding angles of **2**. While the anges at the double bond, e.g., $\theta(C_2C_3C_4)$, were not significantly different for **1** and **2**, the angle at the adjacent carbon C_2 was 12° smaller in **1** as compared to **2**.

Our calculated frequencies showed that the double bond is somewhat more strained in **1** consistent with the longer bond length. The calculated C=C stretch for **2** is 1689 cm^{-1} after scaling by 0.9 in comparison to an experimental value of 1665 cm^{-1}. The trans isomer **1** has a scaled C=C stretch of 1619 cm^{-1} as compared to the experimental value of 1590 cm^{-1}.

Both the geometries and frequencies suggest that **1** is considerably more strained than **2**. The value for ΔE (**1**–**2**)[14] at the SCF level is 32.1 kcal/mol, while the energy difference decreased to 27.1 kcal/mol when a correlation correction (MP2)[14] is included. The experimental activation energy for the conversion of **1** to **2** is 26.4 kcal/mol[1] with **3** postulated as the reaction intermediate.


3

The thermal isomerization of a model compound, *cis*-2,3-dimethylcyclopropane,[15] to the trans isomer has E_a = 61.2 kcal/mol. Subtraction of ΔE(**1**–**2**) from this value gives an estimated E_a for the conversion of **1** to **2** of 34 kcal/mol (assuming no additional stabilization of the transition state **3**). This is in reasonable agreement with the experimental E_a.

The presence of a twist–bent carbon–carbon σ bond in **1** can best be studied in a valence bond framework, i.e., with the use of localized orbitals.[16] We employed our optimum geometry and determined the wave function at the STO-3G level.[17] The wave function was then localized by using the Boys criteria.[18] A GVB-PP[19,20] calculation splitting the C_1–C_6 bond pair was also performed in order to examine the localized orbital obtained from energetic considerations.

Consider that the cyclopropane ring defines the *xz* plane with C_7 along the *x* axis. Then a bent σ bond will consists of 2s, $2p_x$, and $2p_z$ orbitals on C_1 and C_6. The $2p_y$ component should be zero if no twisting is present. Any $2p_y$ component (due to the C_2 symmetry) will lead to twisting of the bond. There is clearly a $2p_y$ component to the orbital determined either as a Boys LMO or as a GVB orbital.[21] For the Boys LMO, the valence orbital coefficients on C_1 are 2s = 0.254, $2p_x$ = 0.207, $2p_y$ = 0.045, and $2p_z$ = 0.500. For the GVB pair, the natural orbital occupancy of the bond orbital is 1.974e and that of the antibonding orbital is 0.026e. The coefficients of C_1 in the GVB bond orbital are 2s = 0.116, $2p_x$ = 0.272, $2p_y$ = 0.070, and $2p_z$ = 0.541. In the energetically determined GVB LMO, the $2p_y$:$2p_x$ ratio is 0.26 showing that there is four times the coefficient to bend the orbital as to twist it.[19] For the Boys LMO, the ratio is slightly smaller, 0.22.

With a hybridization of $sp^{4.8}$ at C_1 and C_6, the twist–bent carbon–carbon σ bond has more p character than the other C–C bonding orbitals of the cyclopropane moiety. The C_1–C_7 (C_6–C_7) bond of **1** has hybridizations of $sp^{2.9}$ at C_1 and $sp^{3.1}$ at C_7. For **2**, the C_1–C_6 bond has hybridizations at C_1 and C_6 of $sp^{2.3}$ and hybridizations at C_1 of $sp^{3.5}$ and C_7 of $sp^{3.4}$ for the C_1–C_7 bond.

The deviation of the centroid of charge for the twist, bent C_1–C_6 bond in **1** (which is in the plane defined by the cyclopropyl carbons due to symmetry) from the C_1–C_6 internuclear axis is smaller than the corresponding deviation in **2** (23.0° and 28.4°, respectively). Since each of the hybridized orbitals in the C_1–C_6 bond in **1** is "twisted" in opposite directions from the plane of the cyclopropane, they will not have as large a projection in the plane. Thus the centroid of charge will be closer to the C–C internuclear axis for a twist, bent σ bond than for a "normal" bent σ bond as was found in the comparison of the C_1–C_6 bonds in **1** and **2**. The LMO for the C_1–C_6 bond at C_1 is twisted by 4.8° above the *xz* plane, whereas at C_6, it is twisted by 4.8° below the plane. For the GVB orbital, the amount of twist above and below the plane is larger, 6.6°. These results are all consistent with the presence of twisting in the C_1–C_6 σ bond to form an "S" shaped (sinusoidal) electron distribution within the bond.[20] Consistent with the highly strained nature of **1**, we found the C_1–C_2 bond in **1** to be quite bent with deviations of the centroid-of-charge from the C_1–C_2 internuclear axis of 17.7° at C_1 and 6.8° at C_2. The corresponding deviations in **2** for this bond are 1.7° and 2.4°.

In summary, theoretical calculations have provided substantial evidence for the existence of a rare type of carbon–carbon σ bonding, which we have catagorized as a twist–bent σ bond.

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[14] SCF: $E(\mathbf{1}) = -270.835\,155$ au, $E(\mathbf{2}) = -270.886\,281$ au; MP-2: $E(\mathbf{1}) = 271.718\,056$ au, $E(\mathbf{2}) = -271.761\,295$ au.

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[20] Geometry optimization at the 3G/GVB level for **1** gives $r(C_1-C_6)$ = 1.531 Å as compared to $r(C_1-C_6)$ = 1.494 Å at 3G/SCF. The 2s coefficient decreases slightly, and the other coefficients show only small changes on optimization.

[21] It is possible that some of the $2p_y$ character in the C_1–C_6 bond is required for orthogonality constraints. However, the $2p_y$ coefficient is comparable to or larger than most of the remaining coefficients on the other atoms.

Synthesis of Main Group Heterocycles by Metallacycle Transfer from Zirconium

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We have been interested in developing new routes to organometallic main group compounds because of their increasing importance in industry as electronic material precursors.[1] Although organozirconium and -titanium reagents have found widespread application in the synthesis of organic compounds,[2] their utility for synthesizing main group compounds has not been fully realized.[3] Here we report the use of the readily available zirconium

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