

Bowlane: Toward Planar Tetracoordinate Carbon

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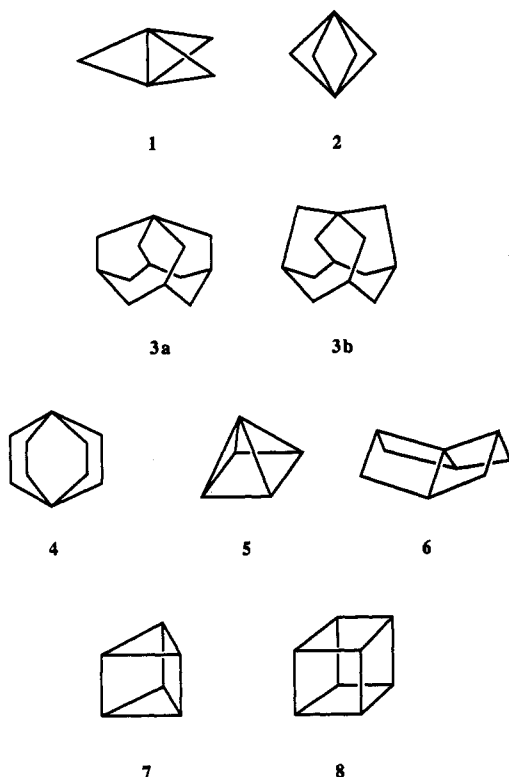
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Ab initio molecular orbital calculations indicate that the $C_{13}H_{20}$ hydrocarbon, bowlane (tetracyclo-[3.3.3.1^{3,10}1^{7,10}]tridecane), has a C_{2v} structure (3b) in which the C-C bonds at the quaternary carbon make angles of 4.6°, 4.6°, 15.9°, and 15.9° with a hypothetical plane perpendicular to the C_2 symmetry axis. A more symmetrical C_{4v} structure (3a) lies 106 kJ mol⁻¹ above 3b and represents the transition structure for inversion at the quaternary carbon.

Introduction

Neutral hydrocarbons containing a tetracoordinate carbon atom with four bonds lying within one hemisphere are rare. The arrangements of the substituents around the central carbon in such cases can be loosely classified as inverted (as, for example, in [1.1.1]propellane (1)) or pyramidal (e.g., [1.1.1.1]paddlane (2)). A limiting case of the latter class occurs when all five atoms lie in the equatorial plane and is referred to as a planar carbon. A small number of hydrocarbons containing inverted carbons have been experimentally characterized.² On the other hand, hydrocarbons containing planar tetracoordinate carbon, although discussed for a long time,³ have not yet been synthesized. The same can be said of pyramidal tetracoordinate carbon.



Recently Dodziuk,⁴ on the basis of molecular mechanics (MM2) calculations, suggested bowlane (tetracyclo-[3.3.3.1^{3,10}1^{7,10}]tridecane) (3), a $C_{13}H_{20}$ isomer, as a possible

synthetic target containing a pyramidal tetracoordinate carbon. Her MM2 calculations indicated a structure with C_{4v} symmetry and a strain energy that was not excessive. However, it is not clear whether calculations such as MM2 that rely on parameterization based largely on normal stable molecules will be reliable for molecules with very unusual structures. Appropriate levels of ab initio molecular orbital theory can be expected to perform better. Accordingly, we have carried out large scale ab initio calculations on bowlane and the results are presented in this paper.

Methods

Standard ab initio molecular orbital calculations⁵ were carried out using the TURBOMOLE^{6,7} and GAUSSIAN 90⁸ programs. HF/STO-3G and HF/6-31G* optimized geometries were obtained subject to specified symmetry constraints and HF/6-31G* harmonic vibrational frequencies were computed analytically. The calculated frequencies enabled the rigorous characterization of stationary points on the surface as equilibrium structures (all real frequencies) or saddle points (one or more imaginary frequencies). Structural parameters referred to in the text are the 6-31G* values. Our 6-31G* calculations used five pure d functions rather than the set of six second-order cartesian gaussians of the standard 6-31G* basis set. Improved relative energies were obtained through calculations on the HF/6-31G* optimized structures using second-order Møller-Plesset perturbation theory with the frozen-core approximation and a variety of basis sets, described in detail below.

Results and Discussion

We note to begin that ab initio calculations on hypothetical synthetic targets ideally should not only determine the structures of the molecules of interest but also should verify that the proposed structures are minima on their potential energy hypersurfaces. This requires the calculation of harmonic vibrational frequencies and has not always been possible in the past because of a lack of efficient programs and computing resources necessary for calculating ab initio molecular force fields for large molecules. In this connection, we have found that several "standard" structures are not located at minima on their potential energy surfaces and thus cannot correspond to equilibrium structures. For example, we find that the structures of D_4 [1.1.1.1] paddlane (2) and D_{4h} [2.2.2.2] paddlane (4), hypothetical hydrocarbons containing py-

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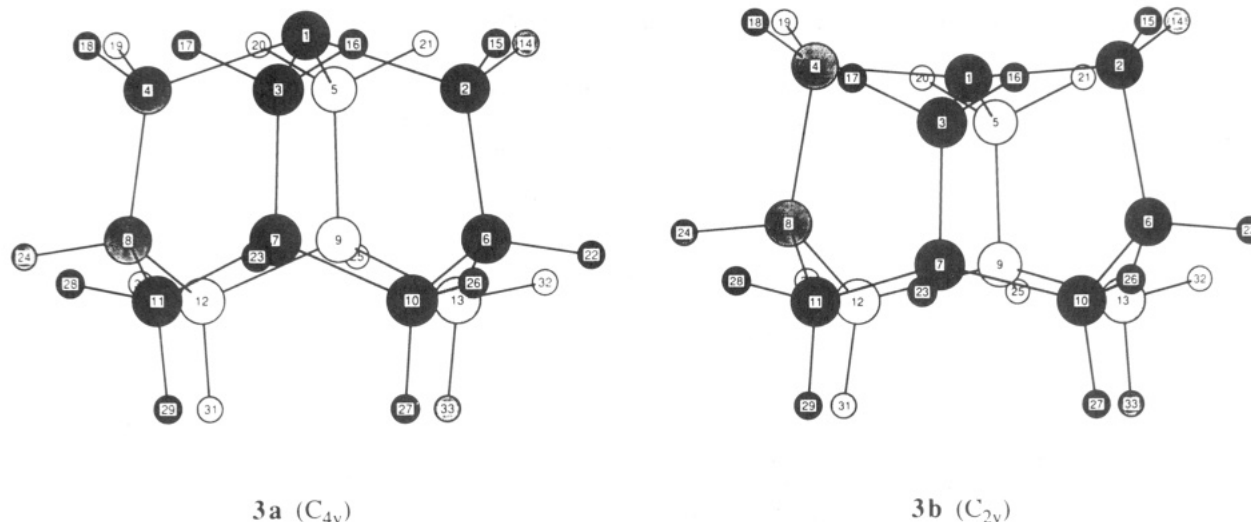


Figure 1. C_{4v} (3a) and C_{2v} (3b) structures of bowlane ($C_{13}H_{20}$).

Table I. Calculated Geometries and Harmonic Vibrational Frequencies for Structures (3a,3b) of Bowlane

geometry ^a				frequencies ^a	
sym	parameter ^b	STO-3G	6-31G*	sym	6-31G*
C_{4v} (3a)	$r(C1-C2)$	1.706	1.716	a_1	3329, 3230, 3202, 3149, 1771, 1652, 1512, 1454, 1225, 1078, 957, 724, 595, 557, 423
	$r(C2-C6)$	1.547	1.522		
	$r(C6-C10)$	1.548	1.536	a_2	3313, 1512, 1484, 1371, 1279, 1184, 1021, 272
	$r(C2-H14)$	1.085	1.076		
	$r(C6-H22)$	1.091	1.090	b_1	3283, 3160, 1658, 1542, 1473, 1381, 1196, 1126, 908, 458, 342, 513i
	$r(C10-H26)$	1.087	1.088		
	$r(C10-H27)$	1.088	1.087	b_2	3357, 3213, 3184, 1631, 1536, 1313, 1184, 1015, 959, 737, 452, 143
	$\angle(C2C1C4)$	140.7	143.0		
	$\angle(C1C2C6)$	118.3	116.3	e	3347, 3296, 3219, 3193, 3153, 1711, 1640, 1538, 1524, 1449, 1418, 1372, 1262, 1215, 1081, 1063, 981, 855, 804, 654, 416, 388, 159
	$\angle(C2C6C10)$	110.7	110.4		
	$\angle(H14C2H15)$	105.2	105.4		
	$\angle(C2C6H22)$	106.4	106.6		
	$\angle(H26C10H27)$	106.9	106.1		
	$\omega(H14C2C6H22)$	57.2	58.4		
	$\omega(H22C6C10H27)$	-82.1	-79.3		
C_{2v} (3b)	$r(C1-C2)$	1.597	1.607	a_1	3317, 3254, 3250, 3209, 3182, 3157, 1778, 1683, 1667, 1552, 1514, 1498, 1457, 1372, 1282, 1204, 1143, 1068, 1021, 844, 737, 713, 679, 617, 471, 412, 284
	$r(C2-C6)$	1.645	1.640		
	$r(C6-C10)$	1.575	1.561	a_2	3336, 3275, 3223, 3187, 1637, 1546, 1495, 1460, 1370, 1344, 1225, 1198, 1154, 1047, 974, 950, 747, 482, 344, 113
	$r(C1-C3)$	1.644	1.655		
	$r(C3-C7)$	1.490	1.473	b_1	3322, 3274, 3224, 3197, 3157, 1728, 1641, 1529, 1508, 1483, 1425, 1351, 1248, 1184, 1146, 1051, 1007, 846, 801, 786, 659, 375, 336
	$r(C2-H14)$	1.087	1.081		
	$r(C6-H22)$	1.092	1.088	b_2	3328, 3254, 3246, 3203, 3175, 1723, 1664, 1554, 1511, 1430, 1416, 1355, 1292, 1251, 1114, 1045, 994, 920, 851, 728, 628, 472, 390
	$r(C10-H26)$	1.088	1.088		
	$r(C10-H27)$	1.087	1.085		
	$r(C3-H16)$	1.079	1.077		
	$r(C7-H23)$	1.089	1.089		
	$\angle(C2C1C4)$	169.3	170.9		
	$\angle(C1C2C6)$	95.6	95.6		
	$\angle(C2C6C10)$	117.2	116.7		
	$\angle(C3C1C5)$	148.4	148.1		
	$\angle(C1C3C7)$	113.8	113.7		
	$\angle(H14C2H15)$	106.6	106.2		
	$\angle(C2C6H22)$	105.6	105.0		
	$\angle(H26C10H27)$	106.4	105.7		
	$\angle(H16C3H17)$	104.9	104.5		
	$\angle(C3C7H23)$	111.9	112.4		
	$\omega(C1C2C6C10)$	-62.7	-63.3		
	$\omega(H14C2C6H22)$	58.1	58.1		
	$\omega(H22C6C10H26)$	41.5	41.7		
	$\omega(H22C6C10H27)$	-73.6	-72.5		
	$\omega(H26C10C6H27)$	115.1	114.2		
	$\omega(H16C3C7H23)$	57.7	58.0		

^a Units: bond lengths (r) in Å, bond angles (\angle) and dihedral angles (ω) in deg, frequencies in cm^{-1} . ^b See Figure 1 for atom numbering.

ramidal centers, are seventh- and fifth-order saddle points, respectively, on their HF/6-31G* potential surfaces.⁹ On

the other hand, we have verified that C_{4v} pyramidane ([3.3.3.3]fenestrane) (5), the simplest possible hydrocarbon with a pyramidal center, is a local minimum on its HF/6-31G* potential surface, as found previously by Minkin et al.¹⁰ using the STO-3G basis set.

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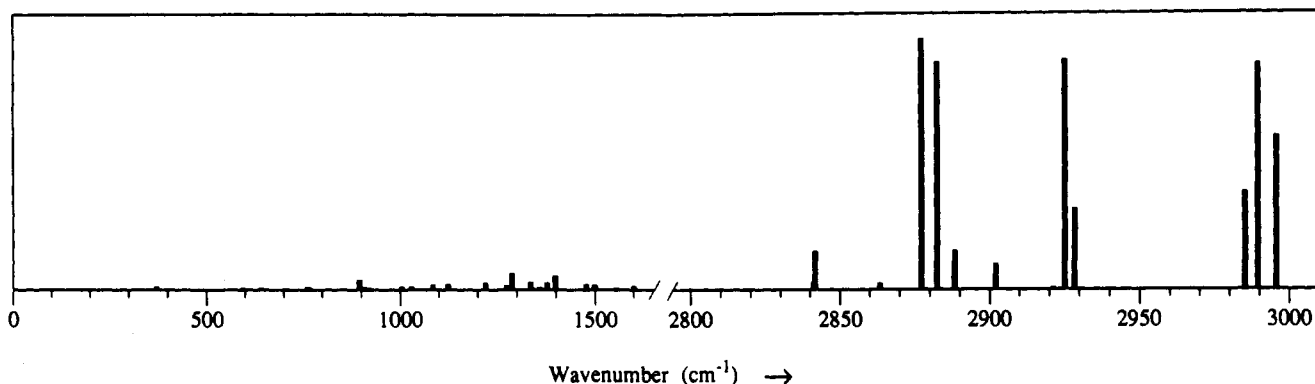
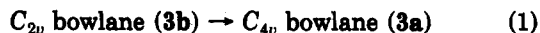


Figure 2. Predicted infrared spectrum of bowlane (3b, scaled HF/6-31G*).

We examined bowlane (3) initially with a C_{4v} symmetry constraint, yielding a structure (3a, Figure 1) whose HF/6-31G* optimized geometry is defined in Table I. The carbon skeleton of 3a resembles crown cyclooctane capped by flattened and elongated pyramidane. The bonds connecting the pyramidal center C1 to its four substituents C2–C5 are very long (1.716 Å), about 0.1 Å longer than the analogous HF/6-31G* bond lengths in pyramidane (1.618 Å) and roughly 0.2 Å longer than typical CC single bonds (1.54 Å). Since the other CC bond lengths in 3a lie within the normal single-bond range, almost all of the bond length strain is borne by C1, on which the lone pair HOMO (highest occupied molecular orbital) is localized. It is not surprising, then, that C_{4v} bowlane is not a minimum on the HF/6-31G* potential surface but a first-order saddle point (see Table I for normal mode frequencies). It connects two equivalent C_{2v} minima, which correspond to the equilibrium structure of bowlane (3b).

The HF/6-31G* optimized geometry of the equilibrium (C_{2v}) structure of bowlane (3b), also defined in Table I and displayed in Figure 1, shows a strain distributed much more evenly throughout its structure. In going from 3a to 3b, the (C1C2, C2C6, C6C10, C10C7, C7C3, C3C1) set of CC bond lengths changes from (1.716, 1.522, 1.536, 1.536, 1.522, 1.716) Å to (1.607, 1.640, 1.561, 1.545, 1.473, 1.655) Å and the HOMO centered on C1 becomes delocalized over C2–C5. The occupancy of the 2p orbital at the quaternary carbon that is oriented along the C_n symmetry axis, i.e., the orbital that corresponds to the lone pair in planar methane, changes from 1.63 to 1.11 electrons during this process. Also, the pyramidane cap opens up considerably, with C2 and C4, in fact, barely crossing the equatorial plane, making angles of 4.6° with it. Since C3 and C5 make angles of 15.9° with the equatorial plane, C1 has bonds on average only 10.2° from the planar carbon limit. For comparison, we find using this measure that the central carbon in D_{2d} windowpane ([4.4.4.4]fenestrane) (6) is further away from the planar carbon limit: 24.8°, based on its calculated structure,¹¹ which we have verified to be a local minimum on the HF/6-31G* potential surface. The corresponding angle in (tetrahedral) methane is 35.3°.

The energy required to interconvert equivalent forms of the equilibrium structure 3b of bowlane via the C_{4v} structure, i.e., the energy change for the process



decreases with increasing size of basis set and with in-

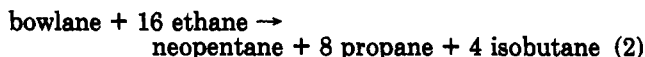
Table II. Calculated Reaction Energies (ΔE , kJ mol⁻¹)^a

	reaction		
	1	2	3
HF/6-31G* ^b	149	-812	-635
MP2/6-31G* ^b	132	-717	-677
MP2/mixed ^{b,c}	106	-703	-659
MP2/6-311+G(2df,p)			-664

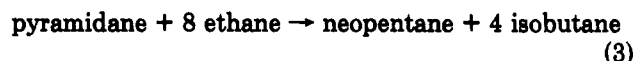
^a Based on HF/6-31G* optimized structures. ^b Sets of five d functions (rather than the standard six for 6-31G*) used. ^c See text for a detailed description of the basis sets.

corporation of electron correlation (see Table II). According to our best estimate, 3b is 106 kJ mol⁻¹ lower in energy than 3a. In contrast, we note that the MM2 calculations⁴ favor a C_{4v} structure over a C_{2v} structure by about 200 kJ mol⁻¹.

The strain energy of bowlane (3b) was calculated as the negative of the enthalpy change ΔH_{298} for the homodesmotic¹² reaction



Initially, the energy change ΔE was calculated at the HF/6-31G* and MP2/6-31G* levels of theory (Table II). Incorporation of electron correlation can be seen to be important. In order to examine the basis set dependence of the MP2 relative energies, a series of calculations was carried out for the corresponding reaction involving the smaller pyramidane molecule (5):



With the (largest) 6-311+G(2df,p) basis set, the MP2 energy change for reaction (3) is -664 kJ mol⁻¹, which may be compared with the 6-31G* value of -677 kJ mol⁻¹. However, using a carefully chosen and consistent mixture of atomic bases, 6-31+G(2d) for the central carbons in pyramidane and neopentane, 6-31+G* for the other pyramidane carbons and for the central carbon in isobutane, and 6-31G* for the remaining atoms, the MP2 reaction energy becomes -659 kJ mol⁻¹, close to the 6-311+G(2df,p) result. We used this economical approach to calculate ΔE for reaction (2) with the following bases: 6-31+G(2d) for the central carbons in bowlane (C1) and neopentane, 6-31+G* for C2–C5 in bowlane and for the central carbon in four of the propane molecules, and 6-31G* for the other atoms. To the resulting ΔE of -703 kJ mol⁻¹ we added a zero-point vibrational energy contribution of 15 kJ mol⁻¹ and a temperature correction term of -5 kJ mol⁻¹ (calculated from experimental^{13,14} vibrational frequencies of all

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species except bowlane, for which the HF/6-31G* harmonic vibrational frequencies of Table I, scaled by 0.9, were employed), yielding ΔH_{298} for reaction (2) of -693 kJ mol^{-1} .

Our estimated strain energy for bowlane of 693 kJ mol^{-1} is large but not out of line with values for known highly strained hydrocarbons of comparable size. For example, the strain energies of [3]prismane (7) and cubane (8) have been estimated to be 622 and 690 kJ mol^{-1} , respectively,¹⁵ and yet 7¹⁶ and 8¹⁷ have both been synthesized. Using our calculated enthalpy change for reaction (2) and experimental¹⁸ heats of formation for all species in this reaction except bowlane, the heat of formation of bowlane, ΔH_{298} , emerges as 492 kJ mol^{-1} . Previous work¹⁹ has shown this type of approach to yield heats of formation for a variety

of strained and unstrained hydrocarbons to within about 13 kJ mol^{-1} .

Finally, the predicted infrared spectrum of bowlane, based on scaled (by 0.9) HF/6-31G* harmonic vibrational frequencies, is shown in Figure 2. The CH stretching modes in the $2800\text{--}3000 \text{ cm}^{-1}$ region are much more intense than the skeletal modes in the ca. $600\text{--}1600 \text{ cm}^{-1}$ region; the latter are weak but probably observable.

Concluding Remarks

The ab initio calculations presented in this paper predict a C_{2v} structure (3b) for bowlane in which the bonds at the quaternary carbon are approaching coplanarity, the average deviation being 10.2° . The calculated strain energy of 693 kJ mol^{-1} is comparable to that of other systems that are highly strained but that have already been synthesized. Our predicted infrared spectrum will hopefully aid in the identification of bowlane during the course of its attempted synthesis.

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Direct Observation of α -Oxo Ketenes from the Photolysis of α -Diazo β -Diketones

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Monitoring by IR spectroscopy of the broad-band irradiation of the symmetrically substituted 2-diazocyclohexane-1,3-dione (11), 3-diazopentane-2,4-dione (19), and 4-diazo-2,2,6,6-tetramethylheptane-3,5-dione (24) in Ar matrices at 12 K showed the formation of 2-carbonylcyclopentanone (*s-Z*-12), acetyl(methyl)ketene (*s-E*-20), and *tert*-butyl(pivaloyl)ketene (*s-E*-25), respectively, in less than 10 min. On increasing the photolysis time to $>3 \text{ h}$, the α -oxo ketenes 12, 20, and 25 decarbonylated to the corresponding oxocarbenes which underwent Wolff rearrangement to carbonylcyclobutane (15), dimethylketene (23), and di-*tert*-butylketene (28), respectively. The reaction of 2-carbonylcyclopentanone (12) with CH_3OH was monitored by IR spectroscopy. Thus, it was found that the reaction started at ca. 100 K and was essentially complete at 140 K, involving the initial formation of the enol form (9) of methyl 2-oxocyclopentanecarboxylate.

Introduction

There has recently been considerable interest in the chemistry of α -oxo ketenes 1.¹ Typical precursors to these species (Scheme I) include dioxinones 2,^{1b-f} furandiones 3,^{1a,j,k} β -keto esters 4,^{1b,i} 2,4-dioxoacids and esters 5,^{1c} acid

chlorides 6,^{1i,2a,b} and α -diazo β -diketones 7.^{2c-f,3,4}

α -Oxo ketenes are highly reactive species and have usually been generated and trapped in situ.^{2b,c,4} A few examples of sterically stabilized α -oxo ketenes that have been isolated include dipivaloylketene,^{1k} *tert*-butyl(pivaloyl)ketene (25),³ and *tert*-butyl(carbomethoxy)ketene.^{2a}

Our group has been actively involved in the studies of these species, and the use of low-temperature FT-IR

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