Structure Determination of 1-Butene by Gas Electron Diffraction, Microwave Spectroscopy, Molecular Mechanics, and Molecular Orbital Constrained Electron Diffraction

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Abstract: The structures and the conformational equilibrium of the CH_3-skew and the CH_3-syn forms of 1-butene were studied by joint analyses of gas electron diffraction and microwave data including constraints taken from ab initio geometry relaxations of the molecule. Electron diffraction data ($s = 3.5$ to $s = 35.25$ Å^{-1}) were recorded on the Balzers KD-G2 unit at the University of Leiden. Microwave data for the parent compound and four monodeuterated species were taken from Kondo, Hirota, and Morino.[4] Ab initio structures of three conformations of 1-butene (skew, syn, and anti) were generated in about 200 h of CPU time (IBM 370/155) by applying our normal coordinate ab initio force relaxation procedure in connection with Pulay's FORCE method on the 4-31G/21G level. In a second series of investigations, data analyses were also combined with molecular mechanics calculations, but the results of MOCED (molecular orbital constrained electron diffraction) were found to agree better with the observed data than the molecular mechanics results. Rotamer populations of CH_3-skew and CH_3-syn at room temperature were found to be 83 and 17%, respectively, corresponding to $\Delta H = 0.53$ (±0.42) kcal/mol. Least-squares analyses have given the following r_g bond lengths (Å): $r(C{=}C) = 1.340$ (4), $r(C_2\text{-}C_3) = 1.502$ (2), $r(C3\text{-}C4) = 1.535$ (2) (CH_3-skew) and 1.526 (2) (CH_3-syn), $r(C_{sp^2}\text{-}H) = 1.104$ (3), $r(C_{sp^3}\text{-}H) = 1.114$ (3). Valence angles (r_z structure) are for CH_3-skew $\sphericalangle C{=}C{-}C = 125.6$ (3)°, $\sphericalangle C{-}C{-}C = 111.7$ (3)°, and for CH_3-syn $\sphericalangle C{=}C{-}C = 127.2$ (3)°, $\sphericalangle C{-}C{-}C = 114.9$ (3)°. Angles involving hydrogen atoms are $\sphericalangle$CCH (in CH_2) = 109.5 (3)°, $\sphericalangle$CCH (in CH_3) = 111.5 (3)°. (No attempt was made here to differentiate between the CH_3-syn and CH_3-skew forms.) This investigation demonstrates that results from high-quality MO calculations can be successfully used as constraints for experimental conformational analyses in which the data are not sufficient to fully determine all the variables of the system studied.

Introduction

Experimental studies of dynamical conformational features are characteristically underdetermined in all but the simplest cases. Interpretations of conformational data are therefore frequently unreliable and seldom quantitative.

In order to alleviate these difficulties in an important area of chemical research, one can make use of hybrid procedures in which joint application is made of various techniques, each providing a different view of reality. Microwave (MW) data, for example, are commonly the basis for deriving r_o or r_s structures.[2] Gas electron diffraction (GED) data provide r_a or r_g structures.[2] If the appropriate corrections are calculated to transform both structure types to a common basis, rotational constants from MW data can be used as constraints in GED data analyses. Such joint GED and MW analyses have been found in many cases to be very powerful[2] in elucidating structural details which could not have been observed in any other way.

If one is willing to invest a few hundred hours of CPU time on a fast computer to refine the structure of a single molecule with four or five first-row atoms, single determinant MO calculations will predict primary structures (bond distances, bond angles, and torsion angles) which are consistently close to experiment and at times even more detailed. The results are not directly comparable to experiment because the calculated values represent equilibrium structures, r_e. But, assuming that calculated differences in equivalent parameters are approximately equal to differences in observed parameters, we can use the results of MO calculations directly to augment experimental conformational analyses. In MOCED (molecular orbital constrained electron diffraction) studies,[3] for example, calculated differences between closely spaced bond distances or bond angles of the same type which are not resolved in the data are used as constraints of GED data analyses, by assuming that $\Delta r_e \simeq \Delta r_a$ for these parameters. The procedure is meaningful, because GED data often contain a great deal of information on the conformational behavior of a molecule which cannot in many cases be deciphered owing to the fact that important primary parameters are experimentally underdetermined. The present study shows that such calculated constraints can also be useful in MW investigations, when the available experimental data are not sufficient to determine the structure of a given molecule completely.

This investigation of 1-butene represents the first example of the simultaneous and consistent application of gas electron diffraction, microwave spectroscopy, and unconstrained ab initio geometry relaxation in a conformational analysis. Since 1-butene is a member of that class of compounds in which empirical molecular mechanical techniques have been found to be somewhat successful, the experimental data were also combined with molecular mechanics calculations in a second series of refinements.

The need for joint procedures in investigating this molecule is obvious. The system possesses 30 degrees of freedom in one conformation (disregarding symmetry), whereas only five or six unknowns can be determined from the electron diffraction data in this case. The microwave data, too, could only be analyzed by including a number of simplifying assumptions, even though data of four monodeuterated species were also available. The results of Kondo et al.[4] are therefore r_o-*like* structures with relatively large error limits.

In addition to testing a procedure of general importance, the present study also describes a conformational problem of particular interest. There is a good deal of evidence that preferred conformations around a double bond involve eclipsing of an atom in an allylic position and that eclipsing of a hydrogen atom is favored over eclipsing of a carbon atom. For 1-butene the enthalpy difference, $\Delta H = H(CH_3\text{-syn}) - H(CH_3\text{-skew})$ (Figure 1), has been estimated[5] on the basis of

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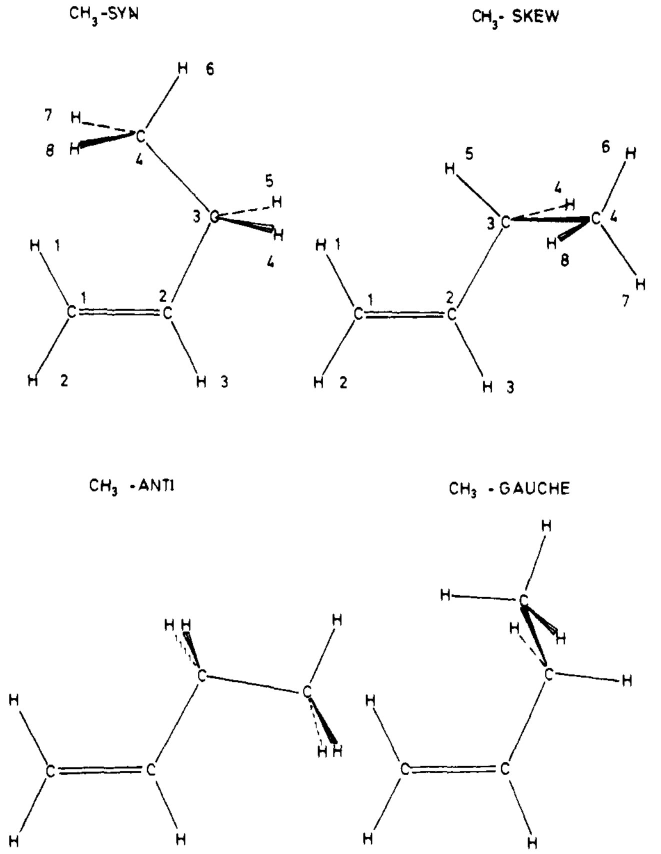

Figure 1. Possible rotamers in 1-butene and numbering of the atoms.

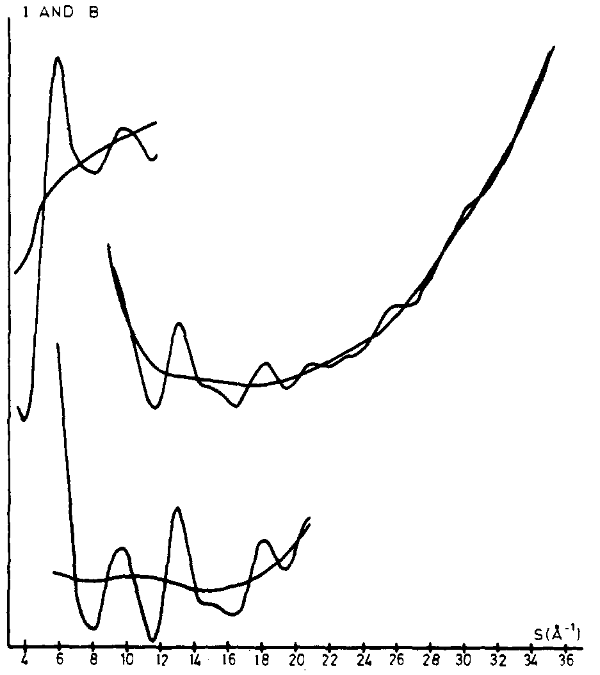

Figure 2. Experimental intensities and final backgrounds for 1-butene.

empirical force field calculations to be 1 kcal/mol. Experimental estimates of this quantity are somewhat at variance with this value. A recent low-temperature matrix infrared study,[6] for example, arrived at a value of ΔH = 240 cal/mol in favor of the CH_3-skew form. Woller and Garbisch[7] concluded that the CH_3-syn form was the most stable rotamer by interpretation of the ^1H NMR spectrum ($\Delta H = -0.100 \pm 0.050$ kcal/mol). This conclusion was questioned by Rummens[8] and by De Haan et al.,[9] who pointed out that differences in the valence angles of the two rotamers, particularly in $H_3C_2C_3$ and HC_3C_2, could influence vicinal coupling constants and, hence, affect this result. The microwave investigation by Kondo et al.[4] gave $\Delta H = 0.15 \pm 0.15$ kcal/mol. In order to comment on this controversy, we have studied the conformational equilibrium of 1-butene by applying the procedures outlined above and described in detail below.

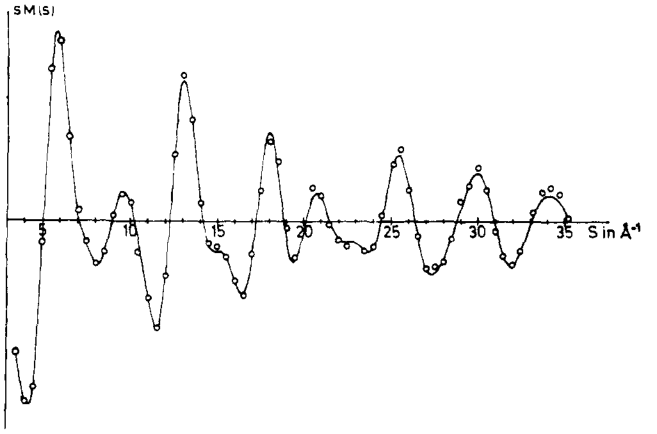

Figure 3. Experimental (dots) and theoretical (solid line) $sM(s)$ curve for 1-butene.

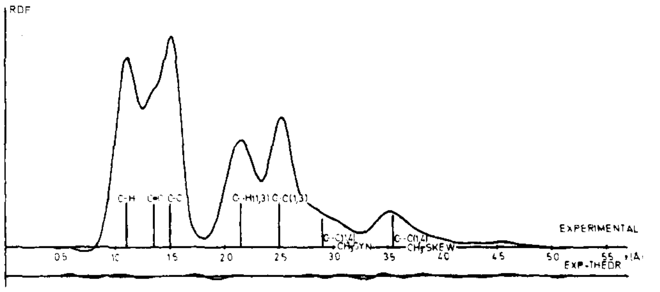

Figure 4. Experimental radial distribution curve for 1-butene and the difference with the calculated one containing a mixture of 83% CH_3-skew form and 17% CH_3-syn form. A damping factor $\exp(-0.002s^2)$ was used. The more important distances are indicated by vertical bars of arbitrary length.

Experimental Section

A commercial sample (Matheson Gas Products) with a purity better than 99% was used. Diffraction patterns were recorded on the Balzers KD-G2 unit of Leiden University. During the experiments a sample pressure of 1.2 atm was used to feed the nozzle system at room temperature. Photographs, taken on Kodak Electron Image Plates, were selected from nozzle-to-plate distances of 59 (two plates), 34 (four plates), and 20 cm (two plates) and measured on an oscillating double beam Joyce-Loebl densitometer. The one-hit model of Foster[10] was employed to convert the density values to intensities. The electron wavelength, corresponding to an accelerating voltage of 40 kV, was calibrated against the known[11] diffraction pattern of benzene, resulting in λ = 0.061 97 Å. The difference between the observed CC distance and the reference value[11] was less than 0.01%.

Further processing of the data by standard procedures[12] gave leveled intensities in the regions

$$59\text{ cm: } 3.50\ \text{Å}^{-1} \leqslant s \leqslant 11.75\ \text{Å}^{-1}$$

$$34\text{ cm: } 5.75\ \text{Å}^{-1} \leqslant s \leqslant 20.75\ \text{Å}^{-1}$$

$$20\text{ cm: } 8.75\ \text{Å}^{-1} \leqslant s \leqslant 35.25\ \text{Å}^{-1}$$

$$\Delta s = 0.25\ \text{Å}^{-1};\ 203\text{ data points}$$

Figures 2 and 3 show the experimental intensities with final backgrounds and $sM(s)$ curves,[13] respectively.

Choice of Rotamers and Vibrational Analysis

The radial distribution function, presented in Figure 4,

Table I. Relative Energies (kcal/mol) of Conformations Possible in 1-Butene Calculated by Molecular Mechanics and ab Initio Methods[a]

	molecular mechanics		ab initio (4-31 G/21 G)	
	rel energy	population, %	rel energy	population, %
CH_3-skew	0	90	0	84
CH_3-syn	0.96	9	0.60	15
CH_3-gauche	2.57	<1		
CH_3-anti	2.63	<1	2.00	~1

[a] The existence of mirror images for the CH_3-skew and CH_3-gauche forms is included ($\Delta S = R \ln 2$) in the computation of the population percentages at room temperature. The total ab initio energy of the CH_3-skew form was −155.864 79 au.

Table II. Calculated and Experimental Vibrational Amplitudes (Å) of 1-Butene[d]

distance	calcd[a]		exptl[c]	no.
	CH_3-skew	CH_3-syn		
C=C	0.042	0.042	0.053 (8)	10
C—C	0.049	0.049	0.056 (5)	11
$C_1 \cdots C_3$	0.068	0.064		
$C_2 \cdots C_4$	0.079	0.073	0.072 (6)	12
C···C (1,4)	0.133	0.101	0.133[b] (skew) 0.101[b] (syn)	
C—H	0.078	0.078	0.087 (4)	13
C···H(1,3)	0.099–0.110	0.098–0.109		
av	0.105	0.105	0.114 (7)	14
C···H rest	0.185	0.143	0.180[b]	
H···H	0.185	0.173	0.180[b]	

[a] Based on the force field[14] and augmented by experimental IR frequencies.[6,15] Averages were calculated including weight factors. [b] Fixed. [c] Derived from joint least-squares analysis of ED and MW data; the two refinements (cf. model considerations) gave practically the same results. Only the u values of the MOCED approach are therefore given. [d] The standard deviations (in parentheses) include a factor of 2.5 to account for correlation effects between the intensities and refer to the last digit. The numbers refer to the correlation Table XI.

Table III. Vibrational Corrections (Å) for 1-Butene[b]

distances independent of torsion	$r_a - r_\alpha$	distances dependent on torsion	$r_a - r_\alpha$
C=C	0.003	C_1—C_4 (CH_3-skew)	−0.011
C—C	0.001_5	C_1—C_4 (CH_3-syn)	0.017
C···C(1,3)	−0.001	C_1H_4; C_1H_5 (CH_3-syn)	−0.014
C—H	0.014	C_1H_5 (CH_3-skew)	0.003
C···H(1,3)	0.006	C_1H_4 (CH_3-skew)	−0.011
C···H(rest)	−0.001	C_2H_6[a]	−0.010
		C_2H_7; C_2H_8[a]	−0.005

[a] In both rotamers. [b] For distances dependent upon torsion see text. For independent distances $r_a - r_\alpha = K_0 - U^2 r_\alpha^{-1}$. The numbering refers to Figure 1.

Table IV. Corrections (10^{-5} cm^{-1}) for the Harmonic Part of the Vibration-Rotation Interaction

	ΔA	ΔB	ΔC
CH_3-skew	159	−3	−7
CH_3-syn	130	−6	−3

Table V. Corrected (A_z, B_z, C_z) Values for the Rotational Constants (cm^{-1})[a]

	normal	1-D	2-D	3-D	4-D
			CH_3-Skew Rotamer		
A_z	0.754 00	0.704 85	0.740 74	0.684 61	0.680 12
B_z	0.138 61	0.133 59	0.130 86	0.137 02	0.137 16
C_z	0.135 23	0.130 82	0.127 45	0.133 44	0.132 72
			CH_3-Syn Rotamer		
A_z	0.511 72	0.477 59	0.506 79	0.481 01	0.477 01
B_z	0.185 89	0.184 00	0.173 29	0.181 96	0.182 56
C_z	0.143 50	0.139 58	0.135 52	0.138 70	0.140 31

[a] Numbers in the naming of the species refer to Figure 1.

shows the existence of two rotamers. Obviously, variation of the torsion angle (C_1C_2-C_3C_4) greatly affects the C_1C_4 distance. The unresolved peak near 2.9 Å corresponds to this distance in the CH_3-syn conformer, while the peak at 3.6 Å corresponds to the analogous distance of the CH_3-skew form. Comparison of the experimental radial distribution function with those based on one single conformation shows a considerable misfit in these regions. Apart from the above-mentioned conformers one might consider two other rotamers: CH_3-anti and CH_3-gauche (see Figure 1). The former can be ruled out because of the absence of a significant peak in the radial distribution function at 3.8 Å. The latter was left out because of its high expected relative energy content (Table I), and because some test refinements including gauche forms yielded unacceptably low mean amplitudes of vibration for the C1-C4 distance.

In order to convert effective rotational constants to zero-point average values, to calculate vibrational amplitudes and $r_a - r_\alpha$ corrections, the force field of Ermer and Lifson[14] was employed.

Mean amplitudes were calculated by using the experimental IR frequencies assigned by Barnes[6] following a procedure described recently by Sellers and Schäfer.[15] Table II lists the derived vibrational parameters.

The calculated values for the $r_a - r_\alpha$ corrections are given in Table III. Corrections to r_α^0 for bond distances were found to be negligible ($<2 \times 10^{-4}$) and the r_α structure was used in the subsequent refinements without further corrections. For distances dependent upon the torsion around C_2–C_3 or dependent upon the torsion of the CH_3 group we applied the formula[16]

$$r_g - r_\alpha = \frac{-kTa_ia_j}{9V_3r_\alpha}\left[-\cos\phi_e + \frac{a_ia_j}{r_\alpha^2}\sin^2\phi_e\right]$$

where V_3 is the threefold potential barrier of rotation, a_i and a_j are the radii of the circles of torsion for the atoms i and j, and ϕ_e is the equilibrium dihedral angle measured from the syn position. Instead of V_3 we used ΔV, the energy difference between a top of the potential energy curve and the adjacent minimum. The same formula can be applied, however. For ΔV we took values from MW[4] for the CH_3 torsion (3.99 kcal/mol for CH_3-syn and 3.16 kcal/mol for CH_3-skew) and from molecular mechanical calculations (Ermer and Lifson[14]) for the C=C—C—C torsion (1.61 kcal/mol for CH_3-syn and 2.60 kcal/mol for CH_3-skew).

Rotational constants in the ground vibrational state (B_0) for the normal as well as for several deuterated species were measured by Kondo et al.[4] In order to use these constants in a joint ED + MW analysis they were corrected for harmonic vibration-rotation interaction,[2a] ignoring electronic interactions.

The corrections, assumed independent of deuteration, as well as corrected values for the rotational constants are listed in Tables IV and V. The uncertainties in the $B_z^{(\alpha)}$ rotational constants were calculated to be 10% of the corrections for the normal and 20% for the deuterated species, by assuming that the errors in the IR frequencies were 5 and 10 cm^{-1}, respectively.

The isotope effect on the r_z structure was determined from

Table VI. Geometries of 1-Butene Rotamers Obtained by Various Methods[a]

	1	2	3	4	5
		CH_3-Skew Rotamer			
$C_1{=}C_2$	1.336	1.319	1.342 (9)	1.346 (5)	1.340 (4)
$C_2{-}C_3$	1.509	1.501	1.493 (8)	1.514 (3)	1.502 (2)
$C_3{-}C_4$	1.532	1.534	1.536 (12)	1.536 (3)	1.535 (2)
$C_1{-}H_1$	1.090	1.073	1.090^b	1.097 (3_5)	1.104 (3)
$C_1{-}H_2$	1.090	1.071	1.090^b	1.097 (3_5)	1.104 (3)
$C_2{-}H_3$	1.090	1.076	1.090^b	1.097 (3_5)	1.104 (3)
$C_3{-}H_4$	1.106	1.085	1.095^b	1.113 (3_5)	1.114 (3)
$C_3{-}H_5$	1.107	1.082	1.095^b	1.113 (3_5)	1.114 (3)
$C_4{-}H_6$	1.106	1.081	1.095^b	1.113 (3_5)	1.114 (3)
$C_4{-}H_7$	1.106	1.081	1.095^b	1.113 (3_5)	1.114 (3)
$C_4{-}H_8$	1.106	1.081	1.095^b	1.113 (3_5)	1.114 (3)
$\sphericalangle C_1{=}C_2{-}C_3$	124.1	125.4	125.4 (2)	123.4 (4_5)	125.6 (3)
$\sphericalangle C_2{-}C_3{-}C_4$	111.3	112.3	112.1 (2)	111.7 (4)	111.7 (3)
$\sphericalangle C_2{=}C_1{-}H_1$	121.9	121.9		117.8 (11)	122.6 (9)
$\sphericalangle C_2{=}C_1{-}H_2$	121.1	121.8		117.8 (11)	122.6 (9)
$\sphericalangle C_1{=}C_2{-}H_3$	120.1	119.2	117.5^c	120.2^b	119.1^b
$\sphericalangle C_2{-}C_3{-}H_4$	108.8	109.1		108.5 (3)	109.5 (3)
$\sphericalangle C_2{-}C_3{-}H_5$	110.0	109.8		108.5 (3)	109.5 (3)
$\sphericalangle C_3{-}C_4{-}H_6$	112.5	110.9	110.3 (8)	112.5 (3)	111.5 (3)
$\sphericalangle C_3{-}C_4{-}H_7$	112.9	110.9	110.3 (8)	112.5 (3)	111.5 (3)
$\sphericalangle C_3{-}C_4{-}H_8$	112.8	110.9	110.3 (8)	112.5 (3)	111.5 (3)
$\phi C_1C_2C_3C_4$	118.4	125.5	119.9 (3)	121.4 (3)	119.9 (3)
method	mol mech	ab initio	MW (ref 6)	MW + ED (MM)	MW + ED (MOCED)
structure		r_e	r_o-like	r_g, r_z	r_g, r_z
		CH_3-Syn Rotamer			
$C_1{=}C_2$	1.337	1.319	1.336 (8)	1.346 (5)	1.340 (4)
$C_2{-}C_3$	1.512	1.503	1.507 (10)	1.514 (3)	1.502 (2)
$C_3{-}C_4$	1.534	1.528	1.536 (6)	1.536 (3)	1.526 (2)
$C_1{-}H_1$	1.089	1.071	1.090^b	1.097 (3_5)	1.104 (3)
$C_1{-}H_2$	1.090	1.071	1.090^b	1.097 (3_5)	1.104 (3)
$C_2{-}H_3$	1.090	1.075	1.090^b	1.097 (3_5)	1.104 (3)
$C_3{-}H_4$	1.106	1.085	1.095^b	1.113 (3_5)	1.114 (3)
$C_3{-}H_5$	1.106	1.085	1.095^b	1.113 (3_5)	1.114 (3)
$C_4{-}H_6$	1.106	1.081	1.095^b	1.113 (3_5)	1.114 (3)
$C_4{-}H_7$	1.106	1.081	1.095^b	1.113 (3_5)	1.114 (3)
$C_4{-}H_8$	1.106	1.081	1.095^b	1.113 (3_5)	1.114 (3)
$\sphericalangle C_1{=}C_2{-}C_3$	126.7	127.0	126.7 (4)	125.8 (4_5)	127.2 (3)
$\sphericalangle C_2{-}C_3{-}C_4$	114.8	115.6	114.8 (5)	115.3 (4)	114.9 (3)
$\sphericalangle C_2{=}C_1{-}H_1$	122.9	122.7		117.8 (11)	122.6 (9)
$\sphericalangle C_2{=}C_1{-}H_2$	120.6	121.3		117.8 (11)	122.6 (9)
$\sphericalangle C_1{=}C_2{-}H_3$	118.8	118.5	118.2^c	119.1^b	118.4^b
$\sphericalangle C_2{-}C_3{-}H_4$	108.2	108.4		108.5 (3)	109.5 (3)
$\sphericalangle C_2{-}C_3{-}H_5$	108.2	108.4		108.5 (3)	109.5 (3)
$\sphericalangle C_3{-}C_4{-}H_6$	112.3	110.4	110.4 (7)	112.5 (3)	111.5 (3)
$\sphericalangle C_3{-}C_4{-}H_7$	113.0	111.2	110.4 (7)	112.5 (3)	111.5 (3)
$\sphericalangle C_3{-}C_4{-}H_8$	113.0	111.2	110.4 (7)	112.5 (3)	111.5 (3)
$\phi C_1C_2C_3C_4$	0	0	0	0	0
method	mol mech	ab initio	MW (ref 6)	MW + ED (MM)	MW + ED (MOCED)
structure		r_e	r_o-like	r_g, r_z	r_g, r_z

[a] Standard deviations (in parentheses) refer to the last digit. They include a factor of 2.5 to account for correlation effects. [b] Assumed. [c] Calculated from planar ethylene configuration and other parameters reported.

the approximate expression[2b]

$$\delta r_z \simeq {}^3\!/_2 a_3 \delta(\langle \Delta Z^2 \rangle) - \delta(\langle \Delta X^2 \rangle + \langle \Delta Y^2 \rangle)/2r_z$$

where δ symbolizes the change due to deuteration of the bond and a_3 the anharmonicity parameter. The difference is -0.0007 ± 0.0012 Å if $a_3 = 2.0 \pm 0.5$ Å^{-1} is assumed. When the influence of the uncertainty in a_3 on the uncertainty in the geometrical parameters was considered, it turned out that the C-H bond length and the CCH valence angles are most affected ($\sim 2 \times 10^{-4}$ Å and $\sim 0.02°$, respectively). Centrifugal distortion, secondary isotope effects, and isotope effects in the valence angles were ignored, since their influence seems negligible for monodeuterated species.[2b]

Model Considerations

The rotamer mixture is far too complex to allow an independent determination of all parameters. Obviously external criteria are needed to limit the number of parameters, to provide us with constraints on the sets of u values, and to provide the differences between certain geometrical parameters. In order to avoid as much arbitrariness as possible we decided to calculate geometries and energies in two different ways: (a) by molecular mechanics using the force field devised by Ermer and Lifson;[14] (b) by ab initio calculations using Pulay's FORCE program[17,18] with the normal coordinate force relaxation procedure by Sellers et al.[19] Each conformation (skew, syn, and anti) was refined without any constraints by about 12–15 cycles. The total computing time spent for these calculations

Table VII. Choice of Geometrical Least-Squares Parameters for 1-Butene, r_1 through r_3, θ_4 through θ_7, and ϕ_8

	par no.	CH_3-skew form	CH_3-syn form
$C_1{=}C_2$	1	r_1	r_1
$C_2{-}C_3$	2	$r_2 - \Delta_2$	$r_2 - \Delta_2$
$C_3{-}C_4$		$r_2 + \Delta_2^1$	$r_2 + \Delta_2$
$(C(sp^2)\text{-}H)_{av}$	3[a]	$r_3 - \Delta_3$	$r_3 - \Delta_3$
$(C(sp^3)\text{-}H)_{av}$		$r_3 + \Delta_3$	$r_3 + \Delta_3$
$\sphericalangle C_1{=}C_2{-}C_3$	4	$\theta_4 - \Delta_4$	$\theta_4 + \Delta_4$
$\sphericalangle C_2{-}C_3{-}C_4$	5	$\theta_5 - \Delta_5$	$\theta_5 + \Delta_5$
$(\sphericalangle C_2{=}C_1{-}H)_{av}$	6[a]	θ_6	θ_6
$\sphericalangle C_1{=}C_2{-}H_3$		$(182.3 - \frac{1}{2}\theta_4)^b$	$(181.6 - \frac{1}{2}\theta_4)^b$
$(\sphericalangle C_2{-}C_3{-}H)_{av}$	7[a]	$\theta_7 - \Delta_7$	$\theta_7 - \Delta_7$
$(\sphericalangle C_3{-}C_4{-}H)_{av}$		$\theta_7 + \Delta_7$	$\theta_7 + \Delta_7$
$\phi C_1C_2C_3C_4$	8	ϕ_8	0

[a] Internal coordinates of this type, the calculated values of which were not significantly different, were grouped together. The Δ values describe the calculated differences between group averages in these cases. [b] This parameter was determined by placing the $C_2{-}H_3$ bond at the angle calculated by ab initio with respect to the line bisecting the $C_1{=}C_2{-}C_3$ angle.

Table VIII. Constraint Differences Δ[a]

	MM approach	MOCED approach
Δ_2	0.011	0.012
$\Delta_2{}^1$	0.011	0.021
Δ_3	0.008	0.005
Δ_4	1.2	0.80
Δ_5	1.8	1.65
Δ_7	2.0	0.99

[a] See Table VII for definition.

was about 200 h of CPU time on the University of Arkansas IBM 370/155. A 4-31G/21G basis set was used with the 4-31G basis[20] on all carbon atoms and the 21G basis[18] on the hydrogen atoms. The calculated parameters were used in the combined (ED + MW) data analysis in agreement with the procedures outlined elsewhere[3] for molecular orbital constrained electron diffraction (MOCED) studies. Table I gives the calculated relative energies and Table VI, columns 1 and 2, the calculated geometries, after complete relaxation.

From a careful consideration of the calculated geometries we derived the following constraints: (1) the CH_3-syn rotamer has C_s symmetry, which is consistent with results from microwave spectroscopy;[4] (2) in both rotamers the arrangement of atoms around the double bond is planar; (3) in both rotamers the methyl groups have C_{3v} symmetry and no tilt is needed; (4) the methylene group retains local C_{2v} symmetry; (5) the CH_3 group is in a staggered position relative to the $C(sp^2)$-$C(sp^3)$ bond.

This led to the choice of geometrical least-squares parameters given in Table VII. Since the values of Δ calculated by molecular mechanics deviated from those calculated by ab initio methods (see Table VIII) we decided to perform two independent refinements: (1) MM approach, combining MW and ED data with fixed Δ values taken from molecular mechanics; (2) MOCED approach, combining MW and ED data with fixed Δ values taken from ab initio (4-31G/21G) calculations. The starting values of the vibrational amplitudes were taken from the force field calculations (Table II). The average $\langle w\Delta^2 \rangle$ of the rotational constants was required to be of the same order as the $\langle w\Delta^2 \rangle$ of the ED data. The relative weights of the rotational constants were taken to be inversely proportional to the squares of their estimated errors (Table IX). The geometrical, vibrational, and conformational parameters were

Table IX. Calculated Rotational Constants (cm^{-1}), Differences (Δ) (10^{-5} cm^{-1}) with B_z Values Derived from Experiment (Table V), and Estimated Errors (10^{-5} cm^{-1}) in These Experimental B_z Values

species		MM approach		MOCED approach		estim error
		B(calcd)	Δ	B(calcd)	Δ	
			CH_3-Skew Rotamer			
normal	A_z	0.754 55	−55	0.753 29	71	16
	B_z	0.138 69	−8	0.138 54	7	3
	C_z	0.135 33	−10	0.135 15	8	3
1-D	A_z	0.705 23	−38	0.704 64	21	32
	B_z	0.134 11	−52	0.133 29	30	5
	C_z	0.130 94	−12	0.130 64	18	5
2-D	A_z	0.740 79	−5	0.740 11	63	32
	B_z	0.131 08	−22	0.130 75	11	5
	C_z	0.127 68	−23	0.127 35	10	5
3-D	A_z	0.685 06	−45	0.684 72	−11	32
	B_z	0.137 32	−30	0.136 89	13	5
	C_z	0.133 32	12	0.133 48	−4	5
4-D	A_z	0.682 01	−189	0.680 15	−3	32
	B_z	0.136 97	19	0.137 06	10	5
	C_z	0.132 99	−27	0.132 53	19	5
			CH_3-Syn Rotamer			
normal	A_z	0.510 22	150	0.512 64	−92	13
	B_z	0.185 71	18	0.186 03	−14	3
	C_z	0.143 34	16	0.143 59	−9	3
1-D	A_z	0.477 72	−13	0.478 44	−85	26
	B_z	0.183 96	4	0.183 80	20	5
	C_z	0.139 65	−7	0.139 50	8	5
2-D	A_z	0.505 70	109	0.507 69	−90	26
	B_z	0.173 19	10	0.173 29	0	5
	C_z	0.135 44	8	0.135 53	−1	5
3-D	A_z	0.479 95	106	0.481 39	−38	26
	B_z	0.181 77	19	0.182 26	−30	5
	C_z	0.138 57	13	0.138 85	−15	5
4-D	A_z	0.475 71	130	0.477 92	−91	26
	B_z	0.182 39	17	0.182 64	−8	5
	C_z	0.140 21	10	0.140 34	−3	5

Table X. Final Values of the Refined Least-Squares Parameters, r_{av} Structure [b]

	parameter	MM	MOCED
1	r_1 C=C	1.342 (5)	1.336 (4)
2	r_2 ⟨C—C⟩	1.521 (3)	1.511 (2)
3	r_3 ⟨C—H⟩	1.086 (3_5)	1.090 (3)
4	θ_4 ⟨C=C—C⟩	124.6 (4_5)	126.4 (3)
5	θ_5 ⟨C—C—C⟩	113.5 (4)	113.3 (3)
6	θ_6 C=C—H	117.8 (11)	122.6 (9)
7	θ_7 ⟨C—C—H⟩	110.5 (3)	110.5 (3)
8	ϕ_8	121.4 (3)	119.9 (3)
9	% skew form	80 (12)	83 (10)
	R value[a]	1.48×10^{-3}	1.23×10^{-3}

[a] $R = (\Sigma w\Delta^2/\Sigma wX^2)^{1/2}$ where X means $(1 + M_{obsd})$ or B_z. [b] The symbol ⟨ ⟩ means not-weighted average. The standard deviations (in parentheses) include a factor of 2.5 to account for the effect of correlation between intensities. Indices of resolution for MM approach: 0.62 (1) (59 cm), 0.81 (3) (34 cm), 0.82 (4) (20 cm). For MOCED: 0.60 (1) (59 cm), 0.83 (3) (34 cm), 0.87 (4) (20 cm).

refined until the calculated standard deviations on the rotational constants were about equal to their estimated errors. When this stage was reached the $\langle w\Delta^2\rangle_{MW}$ was 3.5×10^{-5} and $\langle w\Delta^2\rangle_{ED}$ was 1.8×10^{-6}.

For the ED data the weights[12] were chosen proportional to s and scaled down at both ends of the s interval. An asymmetry parameter $\kappa = 2.0 \times 10^{-5}$ Å^{-3} was used for C-H only.

Results of the Refinements

Table IX shows the resulting calculated rotational constants as well as the differences with B_z values derived from the MW experiment and the estimated errors in the latter B_z values.

The agreement is reasonable, particularly because the MW rotational constants were not corrected for rotation of the asymmetric ethyl group. No general theory for this has been developed. The estimated errors in B_z(exp), in which this uncertainty is left out, are probably too small.

Final values for the refined geometrical parameters (r_{av} structure) are presented in Table X and for the vibrational amplitudes in Table II.

Since the molecular mechanics correlation coefficients hardly differ from those of the MOCED analysis, only the latter are given (Table XI).

Discussion

The best estimate of the energy difference between the CH_3-skew form and the CH_3-syn form is 0.53 kcal/mol, with upper and lower limits of about 0.95 and 0.11 kcal/mol. In calculating ΔH from the concentrations of conformers measured, potential differences in rotational and vibrational entropies for the two conformers were neglected. However, the existence of mirror images for the CH_3-skew form is included ($\Delta S = R \ln 2$). The experimental determinations of ΔH (from IR, MW, and ED) agree with each other and with the energy difference calculated ab initio. The value obtained from the force field calculations seems somewhat too high.

The two least-squares r_{av} structures are converted to r_g, r_z structures via $r_g = r_{av} + K_0$; the perpendicular amplitudes were calculated from the Ermer and Lifson force field[14] as K_0(C-H) = 0.019 Å, K_0(C-C) = 0.003 Å, and K_0(C=C) = 0.004 Å. Geometries (r_g, r_z) are presented in Table VI, columns 4 and 5.

The error limits on the individual bond lengths and valence angles, as opposed to the standard deviations, must include the uncertainties in the conversion from r_{av} to r_g, r_z as well as the uncertainties due to the applied constraints. Since the effects of these various uncertainties are difficult to ascertain we have estimated the error limits on the (r_g, r_z) geometrical parameters (columns 4 and 5, Table VI) to be two times the standard deviations on the r_{av} parameters, i.e., five times the least-squares standard deviations.

Comparison between our r_g, r_z values (Table VI, columns 4 and 5) and the molecular mechanics results (Table VI, column 1) is hampered by the fact that a precise definition of the latter structure type is lacking. Assuming that the parametrization of the force field is such as to produce a structure somewhere between r_g and r_a, the agreement is satisfactory. Also, direct comparison with the values obtained by ab initio methods (Table VI, column 2) is difficult because of the difference in structure definition and our lack of knowledge of the effect of anharmonicity.

It is interesting to note that Tokue et al.[16,21] found that the r_g value of a C=C double bond increases by 0.004 Å per hydrogen atom replaced by a methyl group. This seems also to hold for replacement by ethyl groups, since 1-butene fits perfectly in the series.

From the R values (Table X) it follows that the MOCED constraints (Table VIII) are better than the MM constraints. Note also the remarkable agreement between the microwave study (r_0-like structure, Table VI, column 3) and our MOCED results.

In conclusion, these results show how a combination of experimental data (ED + MW) with constraints taken from ab initio calculations forms a powerful basis with which to arrive at an accurate structure determination for small to "medium-sized" molecules.

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Table XI. Correlation Coefficients (×100) among Refined Parameters from MOCED Refinement[a]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	100													
2	−50	100												
3	−5	−52	100											
4	26	−11	−10	100										
5	−15	−25	30	−91	100									
6	−49	6	−17	30	−26	100								
7	−16	−37	2	−35	53	−8	100							
8	7	−1	56	16	−18	−53	−12	100						
9	13	−2	−3	3	−3	−6	−6	0	100					
10	23	−23	6	6	1	−8	3	0	0	100				
11	33	−24	−1	9	−2	−12	2	−2	0	62	100			
12	6	−2	1	−2	3	−6	−2	1	7	4	4	100		
13	0	7	−9	0	−3	0	−2	−3	4	41	16	0	100	
14	8	−2	−4	5	−5	0	−5	−3	−18	0	−3	11	1	100

[a] See Tables II and X for the numbering of the parameters.

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Supplementary Material Available: List of values of intensity (I), background (B), $1 + M_{\mathrm{obsd}}$, and $1 + RM_{\mathrm{calcd}}$ as a function of s for three s regions, and Cartesian coordinates of the refined ab initio structures of the syn, skew, and anti forms (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Antwerp; (b) University of Arkansas.

(2) (a) K. Kuchitsu in "Molecular Structures and Vibrations", S. J. Cyvin, Ed., Elsevier, Amsterdam, 1972, Chapter 12; (b) K. Kuchitsu and K. Oyanagi, *Faraday Discuss. Chem. Soc.*, **62**, 20 (1977).

(3) N. S. Chiu, H. L. Sellers, and L. Schäfer, *J. Am. Chem. Soc.*, in press.

(4) S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **28**, 471 (1968).

(5) O. Ermer and S. Lifson, *Tetrahedron*, **30**, 2425 (1974).

(6) A. J. Barnes and J. D. R. Howells, *J. Chem. Soc., Faraday Trans. 2*, **69**, 532 (1973).

(7) P. B. Woller and E. W. Garbisch Jr., *J. Org. Chem.*, **37**, 4281 (1972).

(8) F. H. A. Rummens, *J. Magn. Reson.*, **6**, 550 (1972).

(9) J. W. De Haan, L. J. M. Van de Ven, A. R. N. Wilson, A. E. Van der Hout-Lodder, C. Altona, and D. H. Faber, *Org. Magn. Reson.*, **8**, 477 (1976).

(10) H. R. Foster, *J. Appl. Phys.*, **41**, 5344 (1970).

(11) K. Tamagawa, T. Iijima, and M. Kimura, *J. Mol. Struct.*, **30**, 243 (1976).

(12) L. Van den Enden, E. Van Laere, H. J. Geise, F. C. Mijlhoff, and A. Spelbos, *Bull. Soc. Chim. Belg.*, **85**, 735 (1976).

(13) These data have been deposited as supplementary material.

(14) O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121 (1973).

(15) H. L. Sellers and L. Schäfer, *J. Mol. Struct.*, **51**, 117 (1979).

(16) I. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, 17, 207 (1973).

(17) P. Pulay, *Mol. Phys.*, 17, 197 (1969).

(18) P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, **101**, 2550 (1979).

(19) H. L. Sellers, V. J. Klimkowski, and L. Schäfer, *Chem. Phys. Lett.*, **58**, 541 (1978).

(20) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(21) I. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **23**, 33 (1974).

Molecular Dynamics of Cis-Trans Isomerization in Rhodopsin

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Abstract: The photochemical properties of the chromophore in the visual pigment rhodopsin are analyzed using INDO-CISD molecular orbital theory and semiempirical molecular dynamics procedures. The molecular orbital calculations, which include restricted single and double excitation configuration interaction, predict a barrierless first excited singlet state potential surface for cis-trans isomerization of the protonated Schiff base chromophore. The molecular dynamics calculations predict that the excited-state species is trapped during isomerization in an activated complex which has a lifetime of ~0.5 ps. This activated complex rapidly oscillates between two components which preferentially decay to form isomerized product (bathorhodopsin) or unisomerized 11-cis chromophore (rhodopsin) within 1.9-2.3 ps. The nature of this activated complex virtually guarantees a quantum yield greater than 0.5 (our calculations predit a quantum yield of 0.57-0.61). Conformational distortion of the lysine residue is predicted to distort the chromophore in bathorhodopsin, preventing it from reaching a planar all-trans conformation. The molecular orbital calculations suggest that the conformational distortion will be concentrated in the C_7-C_{10} and/or C_{12}-C_{15} regions of the chromophore. Bathorhodopsin is predicted to have a free energy approximately 14 kcal/mol higher than that of rhodopsin due to compression of the lysine residue. The presence of a counterion near the $C_{15}{=}N_{16}$ group in rhodopsin will increase the free energy of bathorhodopsin by ~12 kcal/mol to yield a relative bathorhodopsin free energy of ~26 kcal/mol above rhodopsin (neglecting the effect of other counterions). The bathochromic shift of the absorption maximum of bathorhodopsin relative to rhodopsin is attributed to the effects of the counterion as well as conformational distortion of the chromophore. We conclude that the classical concept that the chromphore in bathorhodopsin has a distorted all-trans geometry is the most realistic model for the first intermediate in the bleaching cycle of rhodopsin.

I. Introduction

The nature of the primary event in vertebrate vision is currently a subject of debate.[2-17] The controversy is focused on the characterization of the first intermediate in the visual cycle, bathorhodopsin (formerly called prelumirhodopsin), and arises from the belief of many investigators that the observed formation time of bathorhodopsin is too fast (<6 ps) to accommodate a 11-cis to 11-trans isomerization of the retinyl polyene.[11-16] Accordingly, a number of alternative mechanisms of bathorhodopsin formation have been proposed which involve proton translocation,[11-16] concerted multibond isomerization,[10] or photochemically induced charge reorganization which results in a trapped (stabilized) protein-chromophore complex.[17] Although all of these mechanisms allow for a rapid (<6 ps) transformation, none adequately accounts for the photochemical equilibrium which can be established among rhodopsin (11-cis), bathorhodopsin, and isorhodopsin (9-cis).

It was, in fact, the observation of the above photoequilibrium that prompted the early suggestion that bathorhodopsin is formed via a cis-trans isomerization yielding a chromophore with an all-trans conformation.[18] This assumption is further supported by the observation that metarhodopsin I, which is known to have an all-trans chromophore, can be photochemically reverted to both rhodopsin and isorhodopsin.[4,19]

This paper reinvestigates the classical picture of the initial step in visual transduction. We demonstrate, using semiempirical all-valence-electron molecular orbital theory and molecular dynamics, that a one-bond photochemical cis-trans isomerization can occur with high quantum efficiency in approximately 2 ps. The molecular orbital calculations, which include restricted single and double excitation configuration interaction, predict a barrierless first excited singlet state potential surface for cis-trans isomerization of the 11-cis protonated Schiff base. The mixing of covalent character into the principally ionic lowest $\pi\pi^*$ singlet state during isomerization

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