Molecular Structure and Conformational Composition of 3,4-Epoxy-1-butene As Determined by ab Initio Molecular Orbital Calculations, Microwave Spectroscopy, and Gas-Phase Electron Diffraction

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The structure and conformational composition for 3,4-epoxy-1-butene have been studied by ab initio molecular orbital calculations at the HF/6-31G* level and a combined least-squares analysis of electron diffraction data and microwave rotational constants. Ab initio calculations showed the presence of three stable conformers, anti, gauche-1, and gauche-2 with the anti form being lowest in energy. The gauche-1 and gauche-2 forms were 0.51 and 2.32 kcal mol^{-1} higher in energy, respectively. Using calculated values for entropies and zero-point and electronic energies of these three forms, a conformational mixture of 76% anti, 22% gauche-1, and 2% gauche-2 was obtained at the experimental temperature of 298 K. The combined electron diffraction and microwave data analysis indicated the presence of both the anti and gauche-1 forms, with a preference for the anti form [64(17)%]. For this model, the experimental values for the geometrical parameters (r_g, $\angle_\alpha$) are as follows (values given for the anti form): r(C−H)$_{av}$ = 1.097(5) Å, r(C$_4$=C$_5$) = 1.331(4) Å, r(C$_3$−O$_1$) = 1.436(2) Å, r(C$_2$−O$_1$) = 1.429(2) Å, r(C$_2$−C$_3$) = 1.477(7) Å, r(C$_3$−C$_4$) = 1.500(7) Å, $\angle$C$_4$C$_3$O$_1$ = 115.2°(19), $\angle$C$_5$=C$_4$C$_3$ = 123.5°(21), ϕCCC=C = 146(12)°.

Introduction

The conformational composition of vinylcyclopropane has been studied extensively and it is well-established that in the gas phase the molecules exist as a mixture of the anti and gauche forms, with the former being lower in energy.[1,2] When one of the carbon atoms in the cyclopropyl group is replaced by an oxygen atom, 3,4-epoxy-1-butene results. Introduction of an oxygen atom disrupts the symmetry of the cyclopropyl group, and the possible conformers for 3,4-epoxy-1-butene can be anti, gauche-1, and gauche-2 (Figure 1).

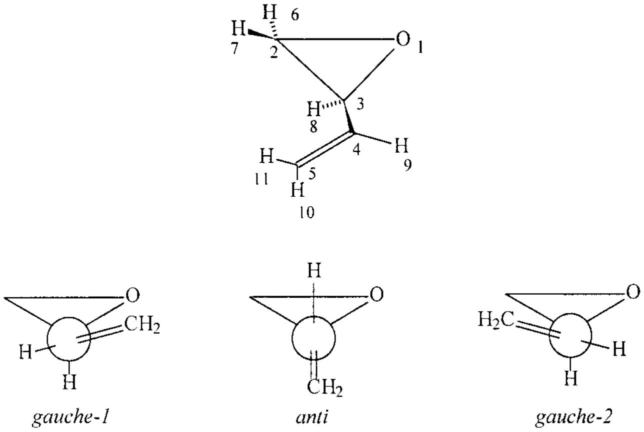

Figure 1. Molecular diagrams with atom numbering.

The conformational composition of 3,4-epoxy-1-butene has been studied by NMR, infrared, Raman, and microwave spectroscopic techniques. The temperature variation of NMR coupling constants[3] has been explained in terms of the presence of one anti and two gauche conformers. The anti form was identified, and three rotational constants were obtained in a microwave spectroscopic investigation of 3,4-epoxy-1-butene.[4] A complete structure determination was not performed. Infrared spectroscopic studies of the solid and gaseous 3,4-epoxy-1-butene and the Raman spectra of all three states[5] confirmed the presence of three conformers, and the energy separations between the most stable anti form and the gauche-2 and gauche-1 forms have been determined in the liquid state to be 1.1 ± 0.2 and 0.8 ± 0.2 kcal mol^{-1}, respectively.

The molecular structure and the vapor-phase conformational composition of 3,4-epoxy-1-butene have not been reported. We have initiated an electron diffraction investigation on the gas-phase structure and conformational composition of 3,4-epoxy-1-butene with aids from microwave rotational constants and ab initio calculations with hope to shed some light on the effect of the oxygen atom on the relative stability of the two possible gauche forms. The results from these studies are reported here.

Experiment and Data Analysis

A sample of 3,4-epoxy-1-butene was obtained from Aldrich (99%) and was used without further purification. Room-temperature electron diffraction data were collected on the Colgate University electron diffraction apparatus at nozzle-to-plate distances of 250 and 100 mm. The accelerating voltage used was 40 keV, and the background pressure was maintained at 1.0 × 10^{-5} Torr during exposure. Exposure times were 50 s for the long and 120 s for the short camera length plates with a beam current of 0.30 μA. Kodak 4 × 5 in. electron image plates were used. Benzene calibration [r_a(C−C) = 1.397(4)A][6] plates were obtained after each experiment under identical conditions as those used for the sample. Four plates from each camera distance were selected for the analysis. The data were collected at intervals of 0.150 mm and corrected for emulsion saturation, plate flatness, and sector imperfections. The intensity data were interpolated at interval units of q [(40/λ) sin(θ/2)] and ranges for the long and short camera experiments were 7 ≤ q ≤ 48 and 25 ≤ q ≤ 125, respectively. Least-squares procedures outlined by Gundersen and Hedberg[7] were followed using elastic scattering factors tabulated by Schaffer, Yates, and Bonham.[8]

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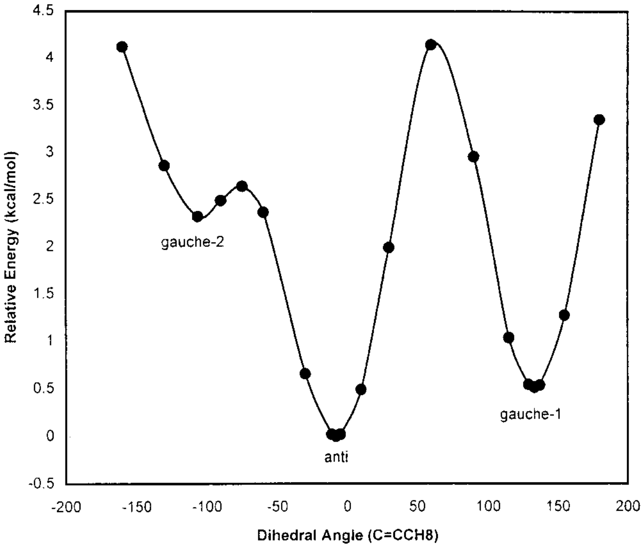

Figure 2. Torsional potential energy function obtained from HF/6-31G* calculations.

TABLE 1: Optimized Geometry (HF/6-31G*) for the Anti, Gauche-1, and Gauche-2 Forms of 3,4-Epoxy-1-butene[a]

	anti	gauche-1	gauche-2
$r(C{-}H)^b$av	1.0777/1.0763	1.0775/1.0758	1.0775/1.0765
$r(C_2{-}O_1)$	1.4002	1.4033	1.4036
$r(C_3{-}O_1)$	1.4073	1.3998	1.4063
$r(C_2{-}C_3)$	1.4577	1.4587	1.4536
$r(C_3{-}C_4)$	1.4828	1.4883	1.4910
$r(C_4{=}C_5)$	1.3183	1.3177	1.3177
$\angle C_2O_1C_3$	62.56	62.72	62.31
$\angle O_1C_2C_3$	58.96	58.53	58.94
$\angle O_1C_3C_2$	58.48	58.75	58.75
$\angle C_4C_3O_1$	116.31	117.40	116.47
$\angle C_2C_3C_4$	121.67	122.18	122.91
$\angle C_3C_4C_5$	123.73	124.16	124.56
$\angle HC_2C_3$	119.15	118.90	119.15
$\angle HC_2O_1$	114.25	114.68	114.43
$\angle HC{=}C_{av}$	121.39	121.05	121.55
$\phi OCC{=}C$	−145.81	−4.99	118.11
$\phi CCC{=}C$	146.54	−73.64	49.70
E^c	0.0	0.51	2.32

[a] Distances in angstroms and angles in degrees. [b] Ring/vinyl averaged values. [c] E = relative energy in kcal mol^{-1}.

Theoretical Calculations. Ab initio molecular orbital calculations were carried out at the HF/6-31G* level using PC Spartan Plus software.[9] Optimized geometries were obtained for the anti, gauche-1, and gauche-2 forms. The anti form was found to be the lowest in energy with the gauche-1 and gauche-2 forms 0.51 and 2.32 kcal mol^{-1} higher in energy, respectively. The torsional potential function about the $C_3{-}C_4$ bond was explored with geometry optimization at 16 fixed dihedral angles, and the results are displayed in Figure 2, which clearly shows the relative positions of these three stable forms. The optimized geometries for the anti, gauche-1, and gauche-2 forms are summarized in Table 1. Frequency calculations were also carried out for the anti and gauche-1 forms.

Vibrational Analysis. A simplified Urey−Bradley force field for 3,4-epoxy-1-butene was determined by fitting the observed vibrational frequencies assigned by Kalasinsky.[5] The frequencies and assignment from ab initio calculations were used as a guide in the analysis. The force constants were refined by using a least-squares analysis program written by Hilderbrandt.[10] The final force field and calculated vibrational frequencies are shown in Table 2. The overall agreement (within 7% of the observed values) is about as good as can be expected for a simple Urey−Bradley model and should be adequate for the calculation of vibrational amplitudes and shrinkage corrections.

TABLE 2

Force Field for 3,4-Epoxy-1-butene[a]

force constant	value	force constant	value	force constant	value
K_{CC}	3.50	H_{CCC}	0.722	H_{torCC}	0.072
K_{CC}	4.60	$H_{C=CC}$	0.699	H_{δ}	0.318
K_{CO}	4.45	$H_{HC=C}$	0.335	F_{CC}	0.359
$K_{C=C}$	5.19	H^r_{HCC}	0.204	F_{CO}	0.299
K^r_{CH}	4.42	H^r_{HCO}	0.370	F_{OH}	0.576
K^v_{CH}	4.40	H^r_{HCH}	0.256	F^r_{CH}	0.844
H^r_{COC}	0.478	H^v_{HCH}	0.169	F^v_{CH}	0.478
H^r_{OCC}	0.366	$H_{torC=C}$	0.663	F_{HH}	0.044
H_{CCO}	0.687				

Calculated and Observed Frequencies for the Anti Form of 3,4-Epoxy-1-butene[b]

assignment	obsd	calcd	assignment	obsd	calcd
CH_2 asym str (vinyl)	3096	3131	CH_2 wag (ring)	1128	1143
CH_2 asym str (ring)	3051	3094	CH_2 bend (ring)	1085	1080
CH str (ring)	3031	3060	CH_2 twist (vinyl)	984	1067
CH_2 sym str (vinyl)	3015	3004	CH_2 wag (vinyl)	967	1056
CH_2 sym str (ring)	3002	2980	C−C str	931	926
CH str (vinyl)	2972	2883	ring def	921	899
C═C str	1651	1561	ring def	822	829
CH_2 def (vinyl)	1465	1515	CH_2 rock (ring)	778	798
CH_2 def (ring)	1443	1483	C−H bend (vinyl)	673	652
CH bend (ring)	1347	1426	ring-C═C bend	458	474
CH bend (vinyl)	1285	1324	ring-C═C bend	330	353
ring breathing	1246	1298	C−C═C bend	295	302
CH_2 rock (vinyl)	1195	1175	torsion	115	115

[a] Stretching force constants have units of mdyn Å^{-1}, bending and torsional force constances have units of mdyn Å, nonbonded Urey−Bradley force constants have units of mdyn Å. Superscript r = oxirane ring and v = vinyl. [b] All the frequencies are in units of cm^{-1}. The observed frequency assignments are quoted from Kalasinsky et al.

Electron Diffraction Analysis. The geometrical parameters chosen to define the model were $r(C{-}H)_{av}$, $r(C_2{-}O_1)$, $r(C_3{-}O_1)$, $r(C_2{-}C_3)$, $r(C_3{-}C_4)$, $r(C_4{=}C_5)$, $\angle O_1C_3C_4$, $\angle C_2C_3C_4$, $\angle C_3C_4{=}C_5$, $\angle HC_2O_1$, $\angle HC_2C_3$, $\angle HC{=}C$, and $\phi C_5{=}C_4C_3O$. It is not possible to determine all the above parameters, and the following assumptions are made to reduced the number of parameters: (a) $r(C_3{-}C_4) - r(C_2{-}C_3) = 0.025$ Å; (b) $r(C_3{-}O_1) - r(C_2{-}O_1) = 0.007$ Å; (c) $\angle C_2C_3C_4 - \angle OC_3C_4 = 5.0°$; (d) $\angle HC_2C_3 - \angle HC_2O_1 = 5.0°$; (e) the planarity of the vinyl group. The numerical differences were obtained from ab initio calculations and are taken as constrain in the analysis.

One-conformer models of the anti and gauche-1 forms were first tested. The results were quite conclusive that neither one of these forms alone could adequately account for the experiment intensity. Figure 3 showed the radial distribution curves from these two one-conformer models. These curves clearly show that a mixture of these two forms would improve the agreement between the model and the data.

A two-conformer model consisting of the anti and gauche-1 forms was employed next. In this model, the theoretical geometrical parameter differences between these two forms were imposed in all refinements. The gauche-2 conformer was not included because the energies from theoretical calculations suggest a population of less than 3%, which is beyond our detection limit. The refined value for the population of the anti form was 67(17)%. The agreement between the model and the experimental data was excellent. The geometrical parameter values from this model are summarized in Table 3.

Combined Electron Diffraction and Microwave Analysis. Rotational constants for the anti form were available in the

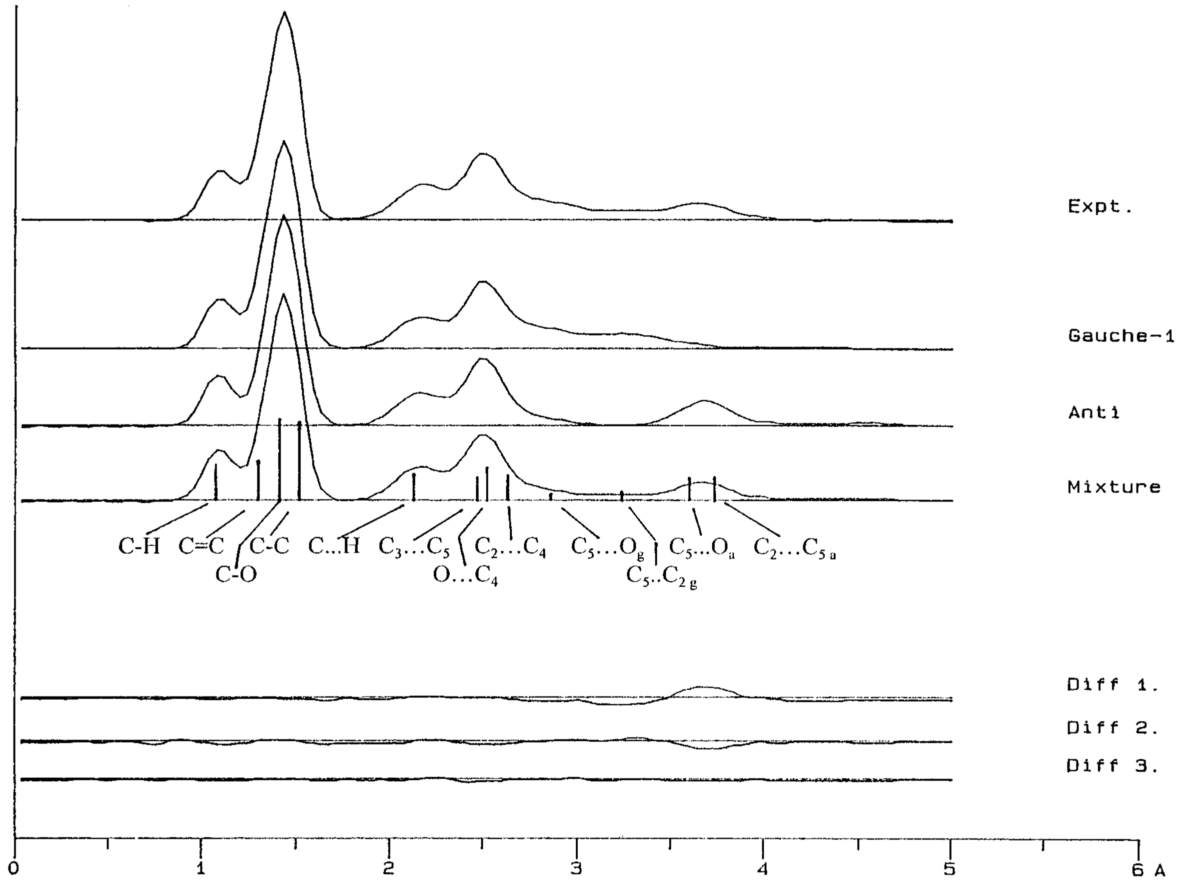

Figure 3. Radial distribution curves for 3,4-epoxy-1-butene. Difference curves are experimental minus theoretical.

literature.[4] We therefore initiated a combined ED/MW analysis of the data. In this model, the anti and gauche-1 forms are included with the populations adjusted by a composition parameter, % anti. The experimental rotational constants of the anti form are included in the analysis after the necessary B_0 to B_z and r_α to r_z corrections are made.[11] A relative weight of 10 000 was given to each of the three rotational constants used in the analysis. The theoretical differences in bond distances and angles between the anti and gauche-1 forms are included as in the two-conformer model. With the inclusion of the rotational constants, the constrains imposed on $r(C_2{-}C_3)$ and $r(C_3{-}C_4)$ were removed, and these parameters were refined simultaneously. The value of the dihedral angle ($\phi C{=}CCC$) was highly correlated to the values of $\angle C{=}CC$ and $\angle CCC$ and refined to values of 145−148(12)°. In the final refinements, the dihedral was fixed at 146°. The agreement between the observed and calculated rotational constants was within 0.2 MHz. The geometrical parameters and the rotational constants for this model are shown in Table 3. A comparison of the combined analysis with the analysis based only on electron diffraction data alone reveals no significant differences in parameters. There is a 3% difference in the population of the anti form. The combined analysis allowed $r(C_2{-}C_3)$ and $r(C_3{-}C_4)$ to be refined independently. The radial distribution and intensity curves corresponding to this model are shown in Figures 3 and 4, respectively.

Discussion

The geometrical parameters for 3,4-epoxy-1-butene obtained from ED/MW least-squares analysis and those for two related compounds are showed in Table 4. The rotational constants from our structure are within 0.2 MHz of the observed values. The

TABLE 3: Structural Parameters for the Anti Form of 3,4-Epoxy-1-butene as Determined by Least-Squares Analysis[a]

	$r/\angle$	l_{ij}	$r/\angle$	l_{ij}
$r(C{-}H)_{av}$	1.096(5)	0.064(4)	$1.097^r/1.098(4)^v$	0.065(5)
$r(C_4{=}C_5)$	1.336(5)	0.0426	1.331(4)	0.0426
$r(C_3{-}O_1)$	$1.439(5)^b$	0.0451	$1.436(2)^c$	0.0466
$r(C_2{-}O_1)$	$1.432(5)^b$	0.0451(39)	$1.429(2)^c$	0.0466(33)
$r(C_3{-}C_2)$	$1.474(10)^b$	0.0451	1.477(7)	0.0466
$r(C_3{-}C_4)$	$1.499(10)^b$	0.0474	1.500(7)	0.0474
$\angle C_4C_3O_1$	116.8(31)		115.2(19)	
$\angle C_5{=}C_4C_3$	121.7(16)		123.1(21)	
$\angle HCO^r$	118.7(26)		117(2)	
$\angle HC{=}C$	120(3)		119(3)	
$\phi C{=}CCO$	146.0		146.0	
% anti	67(17)		64(17)	
method	ED^b		ED/MW	
	Dependent Parameters			
$r(C4\cdots O1)$	2.487(28)	0.067(6)	2.476(16)	0.071(5)
$r(C3\cdots C5)$	2.477(29)	0.0676	2.477(23)	0.071
$r(C5\cdots O1)_a$	3.645(12)	0.0981	3.636(8)	0.0981
$r(C5\cdots O1)_g$	2.844(30)	0.119	2.833(24)	0.119
$r(C5\cdots C2)_a$	3.740(14)	0.0943	3.732(13)	0.0943
$r(C5\cdots C2)_g$	3.228(31)	0.141	3.214(30)	0.141

B_o(obsd)	B_z(obsd)	B_z(calcd)
17367.285	17402.955	17403.0
3138.219	3135.903	3135.08
30443.686	3044.093	3044.50

[a] Two-conformer models. Distances(r_g) in angstroms and angles($\angle_\alpha$) in degrees; values in parentheses are 2σ error estimations which included systematic error; superscript r and v indicate the oxirane ring and the vinyl group, respectively; subscript a and g refer to anti and gauche-1 forms, respectively. Rotational constants in MHz. [b] $r(C_3{-}O_1) = r(C_2{-}O_1) + 0.007$ Å and $r(C_3{-}C_2) = r(C_3{-}C_4) - 0.025$ Å are assumed. [c] $r(C_3{-}O_1) = r(C_2{-}O_1) + 0.007$ Å is assumed.

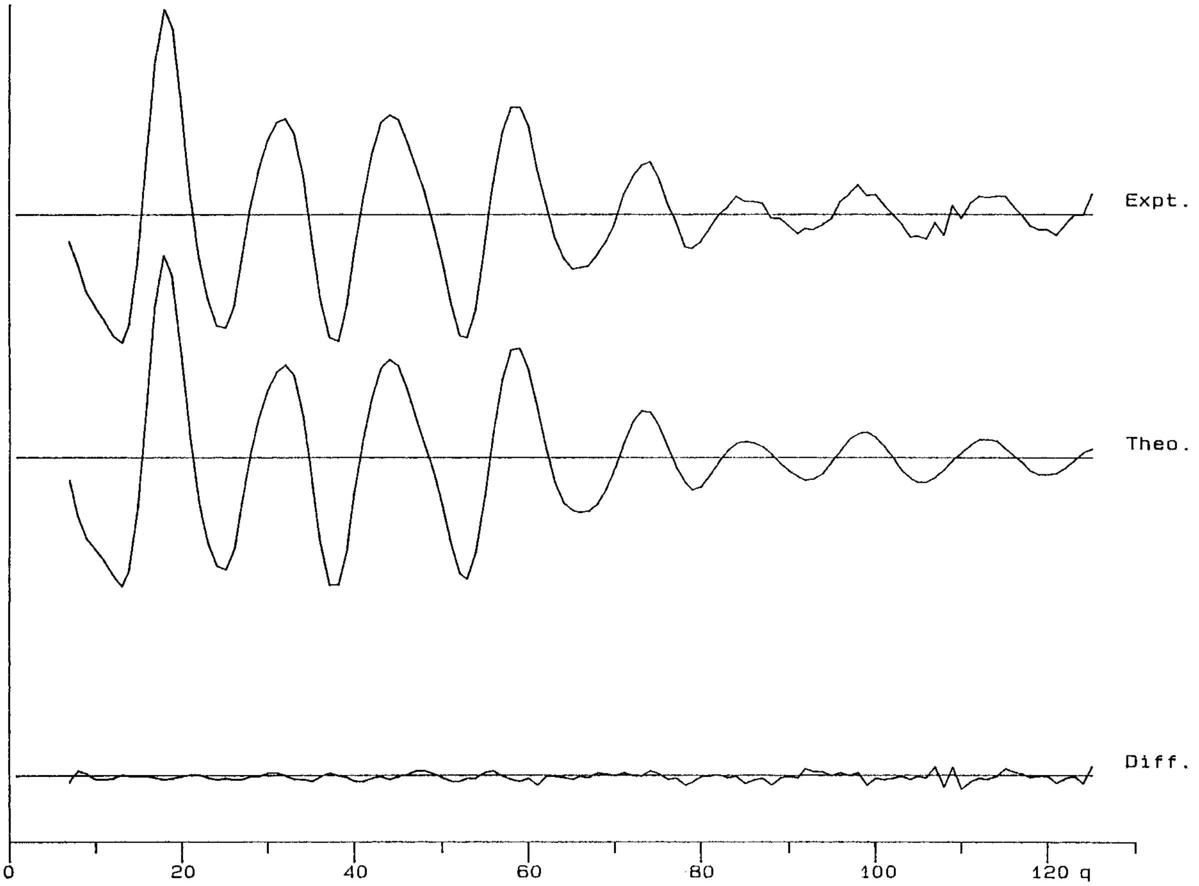

Figure 4. Intensity curves for 3,4-epoxy-1-butene from the ED/MW combined least-squares analysis.

TABLE 4: Comparison of Experimental and Theoretical Geometrical Parameter Values Obtained for 3,4-Epoxy-1-butene and Related Molecules[a]

	ethylene oxide		propylene oxide		3,4-epoxy-1-butene	
	exptl	theor	exptl	theor	exptl	theor
r(C−O)	1.431(2)	[1.402]	1.436(ass)	[1.404]	1.429/ 1.436(2)	[1.400/ 1.403]
r(C−C)	1.466(2)	[1.453]	1.471(ass)	[1.453]	1.477(7)	[1.458]
r(C−C$_M$)			1.513(20)	[1.505]		
r(C−C$_V$)					1.500(7)	[1.483]
∠CCC$_M$			120.9(10)	[122.56]		
∠CCC$_V$					123.1(21)	[123.73]
method	MW		MW		ED/MW	
ref	13		14		this work	

[a] Distances in angstroms and angles in degrees; M = methyl group, V = vinyl group; bracketed values are ab initio HF/6-31G* results.

vinyl oxirane and ethylene oxide structures are very similar. It appeared that the C−C bond in the ring is slightly longer as a result of the vinyl substitution. Calculations also showed that the C_3-O_1 bond is longer than the C_2-O_1 bond (0.0072 Å) upon vinyl substitution. The C−O bond in the ethylene oxide is 0.015 Å longer than that reported for dimethyl ether (1.415(1) Å).[12] The exocyclic C−C bond length is longer in propylene oxide than in 3,4-epoxy-1-butene. Ab initio calculations at the HF/6-31G* level showed that the exocyclic C−C bond in propylene oxide is 0.022 Å longer than that in 3,4-epoxy-1-butene. If this difference is assumed, the experimental C−C bond length from 3,4-epoxy-1-butene (1.500 Å) would predict a C−C bond of 1.522 Å in propylene oxide, and the estimated value from an early microwave investigation reported a value of 1.513(20) Å.

The least-squares analysis of the experimental electron diffraction data showed rather convincingly that the 3,4-epoxy-1-butene molecules exist as a mixture of two conformers, anti, 67(17)%, and gauche-1, 33%. This result is consistent with those from ab initio calculations which show 3,4-epoxy-1-butene exists as a mixture of three conformers with the anti form being the most stable and the gauche-2 being the least stable. From the calculated relative energies (electronic and zero-point) and entropies, standard Gibbs free energies and the populations of the three forms can be calculated. The populations at the experimental temperature of 298 K were 76% anti, 22% gauche-1, and 2% gauche-2. The relative stability of the two gauche forms may be the result of steric repulsion between the vinyl proton and the CH$_2$ protons in the oxirane (in gauche-2 form) and/or the attractive force between the vinyl proton and the oxygen lone pairs (in gauche-1 form). The vinyl group in the gauche-2 form is farther away from the CH$_2$ group of the oxirane (ϕCCC=C = 49.7°) than the vinyl group in gauche-1 from the O atom of the oxirane (ϕOCC=C = 4.99°). The closest vinyl proton and oxygen distance has a value of 2.47 (20) Å (ab initio value = 2.56 Å) in the gauche-1 form. It is tempting to attribute (a) the 40° difference in the torsional angles between the gauche-1 and gauche-2 forms and (b) the stability of the gauche-1 form (1.8 kcal/mol) to the presence of a hydrogen-bonding-like [H−O···H] interaction. Close examination of the calculated terminal vinyl C−H bond lengths showed that the rC−H$_{11}$ (proton pointing toward the oxygen atom) bond is slightly longer than the rC−H$_{10}$ bond (1.0750 Å vs 1.0744 Å). Ab initio calculations carried out for vinylcyclopropane, at the HF/6-31G* level, showed that the ϕCCC=C dihedral angle (48.09°) of the gauche form, where interaction between the vinyl proton and the CH$_2$ protons of the cycloporpyl group is possible, is very similar to the value calculated for the gauche-2 form in 3,4-epoxy-1-butene (49.7°). The ϕOCC═C dihedral angle of 4.99° in the gauche-1 form is indeed unusually small and perhaps may be a indication of the presence of an attractive force between the O atom and the vinyl proton.

Supporting Information Available: A correlation matrix for parameters is given. This material is available free of charge via the Internet at http://pubs.acs.org.

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