A Comparative Molecular Orbital Study
on the Low Lying Singlet and Triplet States
of Ethylene Oxide

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Two cross sections of the energy hypersurface for the ethylene oxide molecule, one involving a ring distortion, the other rotation about the C–C bond, have been studied by the semi-empirical and non-empirical SCF molecular orbital methods. The results indicate a ring distorted equilibrium geometry for the excited states of the molecule and implicate the lowest triplet state as an intermediate in the $C_2H_4 + O(^3P) \rightarrow$ ethylene oxide reaction.

The results of the various types of calculations are compared.

Key words: Ethylene oxide — Low-lying singlet and triplet states of ~

1. Introduction

Low lying excited electronic states can profoundly influence the chemistry of the ground electronic state and may be directly involved in thermal and photo-chemical transformations. For example, the common reactive intermediate in the episulfide-forming addition of ground, triplet state sulfur atoms to olefins and the thermal and photochemical decomposition of episulfides appears to be the lowest excited triplet state of the episulfide molecule. It is of special significance with regard to the stereochemical aspects of these reactions that this lowest excited triplet state has a ring distorted equilibrium geometry which features a substantial energy barrier for rotation about the carbon-carbon bond [1]. Theoretical studies on aziridine [2] have also pointed to a ring distorted geometry in the lowest excited triplet state.

In the present study we have explored the ground and low lying excited states of the ethylene oxide molecule. The close similarities between the experimental kinetic data for the sulfur atom plus olefin and oxygen atom plus olefin systems [3] suggest analogous electronic manifolds of the episulfide and epoxide molecules and for this reason we considered the variation of the CCO bond angle (α) and the internal rotation about the C–C bond (θ) in the epoxide molecule as the two most relevant internal coordinates in the addition-decomposition sequence:

Scheme 1
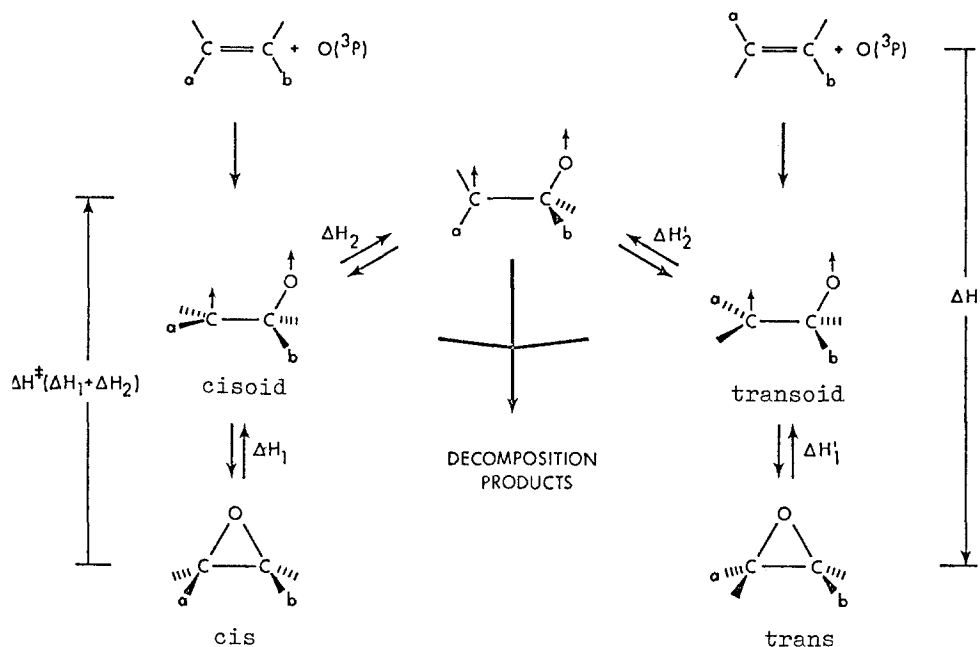
Consequently we generated two cross sections of the molecular energy hyper-surface, $E = E(\alpha)$ and $E = E(\theta)$ for the ground and several low lying excited states.

2. Computational Method

Semi-empirical MO calculations were carried out at three levels of approximations corresponding to the Extended Hückel MO (EHMO), the Complete Neglect of Differential Overlap (CNDO) and the Intermediate Neglect of Differential Overlap (INDO) methods. It should be noted that the EHMO method

Table 1. Contracted Gaussian basis sets used in the calculations of ethylene oxide

Basis set	Chemical system	Basis set size		Basis set type	Ref.
		Primitive	Contracted	Primitive → Contracted	
A	O	17	5	$(8^s, 3^p)$ → $[2^s, 1^p]$	[5]
	C	17	5	$(8^s, 3^p)$ → $[2^s, 1^p]$	[5]
	H	3	1	(3^s) → $[1^s]$	[5]
	C_2H_4O	63	19	$19\,sp$	—
B	O	24	10	$(9^s, 5^p)$ → $[4^s, 2^p]$	[6]
	C	24	10	$(9^s, 5^p)$ → $[4^s, 2^p]$	[6]
	H	4	2	(4^s) → $[2^s]$	[6]
	C_2H_4O	88	38	$38\,sp$	—

does not take into consideration spin-spin interaction and yields only the arithmetic mean of excited singlet and triplet states.

Non-empirical MO calculations were carried out within the Roothaan-Hartree Fock framework [4] using two different Gaussian basis sets, specifications for which are summarized in Table 1. The excited state energies were computed by Roothaan's virtual orbital technique [4] for the non-empirical MO methods.

3. Results and Discussion

The two basis sets used in the present *ab initio* study imply different quality representations and it appeared instructive to compare the computed total energies with the Hartree Fock Limit (HFL) as well as with previously reported values. The relevant data are summarized in Table 2. The total energy values

Table 2. The breakdown of total energy to experimental and theoretical components for ethylene oxide and its constituent atoms

A. Data for the constituent atoms of C_2H_4O (Hartree)

Atom	E_{HF}[a]	E_{corr}[b]	E_{rel}[c]	Sum for C_2H_4O
C	− 37.6886	−0.1581	−0.0138	− 75.7210
O	− 74.8093	−0.2575	−0.0494	− 75.1162
H	− 0.5000	—	—	− 2.0000
Sum for C_2H_4O	− 152.1865	−0.5737	−0.0770	− 152.8372

[a] Reference [7].
[b] Reference [8].
[c] Reference [9].

B. Data for ethylene oxide

Experimental components	E (Hartree)	Theoretical component	E (Hartree)
Total atomic energy	− 152.8372[a]	Hartree-Fock energy[f]	− 152.9518
Dissociation energy	− 0.9927[b]	Correlation energy[e]	− 0.8570
Zero-point energy	− 0.0559[c]	Relativistic energy[d]	− 0.0770
Experimental energy	− 153.8858	Total energy	− 153.8858

[a] Given as the final sum in Table 2A.
[b] Calculated from the heats of formation [10].
[c] Calculated as $E_{ZPV} = \frac{1}{2}hc\Sigma_{i=1}^{15}\bar{v}_i$ where $\bar{v}$ are the fifteen fundamental vibrations (in units of cm^{-1}) as taken from Ref. [11].
[d] Assumed to be equal to that of the atomic relativistic energy (E_{rel} in Table 2A).
[e] The molecular correlation energy of C_2H_4O was calculated as the following sum:

$$E_{corr}(CH_2 = CH_2) + E_{corr}(O) + \Delta E_{corr}(bond) = -0.534 - 0.258 - 0.065 = -0.857 \text{ Hartree}$$

[f] The Hartree-Fock Limit was estimated as $E_{HF} = E_{exp} - (E_{corr} + E_{rel})$.

resulting from the present work and those from previously reported studies are given in Tables 3 and 4, respectively.

The two cross sections of the energy hypersurface, $E = E(\alpha)$ and $E = E(\theta)$, as calculated by the three semi-empirical MO methods are tabulated in Tables 5 and 6, respectively, and the potential energy curves are illustrated in Fig. 1.

As seen from Fig. 1 the EHMO method gives an incorrect geometry for the ground state and its prediction for the rotational energy barrier in the lowest

Table 3. Computed energies of ethylene oxide in its equilibrium geometry with different basis sets

M.O. number	Orbital symmetry	Molecular orbital energy (Hartree)	
		A	B
1	1σ	$-$ 20.66121	$-$ 20.55791
2	2σ	$-$ 11.39367	$-$ 11.29956
3	3σ	$-$ 11.39363	$-$ 11.29881
4	4σ	$-$ 1.39803	$-$ 1.42594
5	5σ	$-$ 0.91958	$-$ 0.93675
6	6σ	$-$ 0.85550	$-$ 0.87224
7	1π	$-$ 0.69707	$-$ 0.71768
8	7σ	$-$ 0.62114	$-$ 0.65432
9	2π	$-$ 0.53714	$-$ 0.55445
10	8σ	$-$ 0.49936	$-$ 0.53969
11	3π	$-$ 0.39723	$-$ 0.45086
12	9σ	$-$ 0.42390	$-$ 0.45046
13	$10\sigma^*$	$+$ 0.37876	$+$ 0.22297
14	$11\sigma^*$	$+$ 0.50015	$+$ 0.23026
15	$12\sigma^*$	$+$ 0.65174	$+$ 0.26556
16	$13\sigma^*$	$+$ 0.66682	$+$ 0.27415
17	$4\pi^*$	$+$ 0.60476	$+$ 0.38767
18	$14\sigma^*$	$+$ 0.69788	$+$ 0.38805
E_{nn}		75.09639	75.09708
$(T + E_{ne})$		$-$ 355.05167	$-$ 356.25292
E_{ee}		127.72836	128.34474
E_{total}		$-$ 152.22688	$-$ 152.81111

Table 4. A comparison of previously published total energy values of ethylene oxide with present values

Source	E (Hartree)
Clark, D. T.: Theoret. Chim. Acta **15**, 225 (1969)	$-$ 151.3951
Bonacorei, R., Scrocco, E., Tomasi, J.: J. Chem. Phys. **52**, 5270 (1970)	$-$ 152.3688
Franchini, P. F., Zandomeneghi, M.: Theoret. Chim. Acta (Berl.) **21**, 90 (1971)	$-$ 152.4880
Hayes, E. F.: J. Chem. Phys. **51**, 4787 (1969)	$-$ 152.6745
Basch, H., Robin, M. B., Kuebler, N. A., Baker, C., Turner, D. W.: J. Chem. Phys. **51**, 52 (1969)	$-$ 152.8012
Present work (Basis set B)	$-$ 152.8111
Hartree-Fock energy	$-$ 152.9518
Experimental energy	$-$ 153.8858

Table 5. Variation of total energies (kcal mol^{-1}) with ring distortion, $E = E(\alpha)$ for the ground and first excited triplet state of ethylene oxide

CCO bond nagle α	EHMO		CNDO		INDO	
	S_0	$1/2(T_1 + S_1)$	S_0	T_1	S_0	T_1
59° 10'	−7646.7	−7470.3	−22391.4	−22197.2	−21520.1	−21334.2
70°	−7663.9	−7523.8	−22327.5	−22197.8	−21460.0	−21359.5
80°	−7668.8	−7568.2	−22257.6	−22192.7	−21393.4	−21355.5
90°	−7668.6	−7590.1	−22200.6	−22188.8	−21338.9	−21351.3
100°	−7664.1	−7593.6	−22172.1	−22189.2	−21311.3	−21350.9
110°	−7654.7	−7594.4	−22132.3	−22182.4	−21270.7	−21343.8
120°	−7639.3	−7583.4	−22127.2	−22174.6	−21263.1	−21335.3
130°	−7618.3	−7564.7	−22130.0	−22162.3	−21263.3	−21322.0
ΔH_1 (kcal mol^{-1})	52.3		193.6		160.6	

Table 6. Variation of total energies (kcal mol^{-1}) with C–C rotation $E = E(\theta)$ for the first excited triplet of ring distorted ethylene oxide

C–C rotational angle at $\alpha_{min}(T_1)$ θ	EHMO $1/2(T_1 + S_1)$	CNDO T_1	INDO T_1
0°	−7594.4	−22197.8	−21359.5
90°	−7595.4	−22202.6	−21355.5
ΔH_2	− 1.0	− 4.8	+ 4.0

Table 7. Variation of total energy for the ground and low lying excited states with angular ring distortion in ethylene oxide as computed with the large basis set (B)

| Geometry	I	II	III	IV	V	VI
CCO Bond Angle	59° 10'	80°	90°	100°	110°	120°
Angular Distortion	0°	20° 50'	30° 50'	40° 50'	50° 50'	60° 50'
$C_1 \dots 0$ (Distorted)	1.436 Å	1.869 Å	2.056 Å	2.228 Å	2.382 Å	2.518 Å
Nuclear Repulsion (Hartree)	75.09708	70.48142	69.07513	68.01601	67.22042	66.63250
Total Energy (Hartree) S_0	−152.81111	−152.77238	−152.74629	−152.72062	−152.69705	−152.67627
Excitation Symmetry Multiplicity						
$7\sigma \rightarrow 10\sigma^\star$ Σ S	−152.18564	−152.33255	−152.36699	−152.38887	−152.39955	−152.40007
T	−152.20633	−152.39340	−152.42118	−152.43270	−152.43385	−152.42922
$2\pi \rightarrow 10\sigma^\star$ π S	−152.28888	−152.41802	−152.42688	−152.42874	−152.42448	−152.41651
T	−152.30658	−152.43524	−152.44125	−152.44088	−152.43492	−152.42704
$8\sigma \rightarrow 10\sigma^\star$ Σ S	−152.27275	−152.47628	−152.49692	−152.48855	−152.47003	−152.44170
T	−152.31475	−152.50299	−152.52978	−152.53616	−152.53817	−152.54299
$3\pi \rightarrow 10\sigma^\star$ π S	−152.37823	−152.55941	−152.60760	−152.62322	−152.62669	−152.62262
T	−152.38463	−152.58018	−152.62777	−152.64129	−152.64211	−152.63488
$9\sigma \rightarrow 10\sigma^\star$ Σ S	−152.36105	−152.44306	−152.47629	−152.50355	−152.53223	−152.57297
T	−152.41771	−152.66560	−152.71490	−152.72643	−152.71293	−152.67380
$3\pi \rightarrow 11\sigma^\star$ π S	−152.41961	−152.30802	−152.29495	−152.27966	−152.27357	−152.27921
T	−152.43968	−152.31293	−152.29869	−152.28286	−152.27631	−152.28164
$9\sigma \rightarrow 11\sigma^\star$ Σ S	−152.39858	−152.35016	−152.34524	−152.33118	−152.31440	−152.29402
T	−152.43490	−152.37360	−152.36471	−152.34881	−152.33079	−152.30870
$3\pi \rightarrow 12\sigma^\star$ π S	−152.36231	−152.30651	−152.28000	−152.26946	−152.26550	−152.27017
T	−152.37478	−152.31591	−152.28601	−152.27462	−152.26996	−152.27397
$9\sigma \rightarrow 12\sigma^\star$ Σ S	−152.33680	−152.34604	−152.33945	−152.32752	−152.31022	−152.28825
T	−152.28146	−152.36577	−152.34933	−152.33574	−152.31651	−152.29285
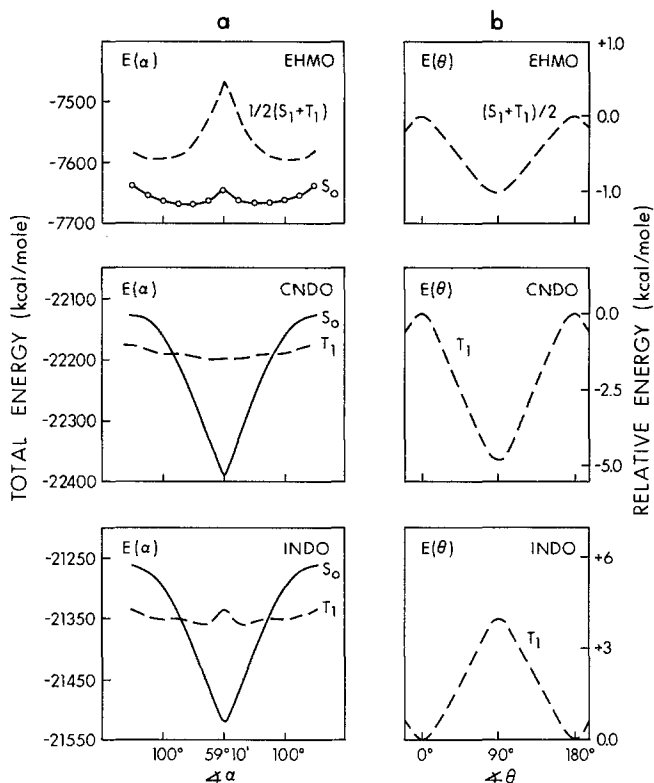
Fig. 1a and b. Calculated total energy variation as a function of (a) CCO angle (α) for the ground (S_0) and lowest triplet (T_1) states, and (b) CC rotational angle (θ) for the lowest triplet state of ethylene oxide using semi-empirical MO methods

Table 8. Variation of total energy of the ground and low lying excited states of ring distorted ethylene oxide with C–C rotational angle (θ) at a CCO angle of 100°

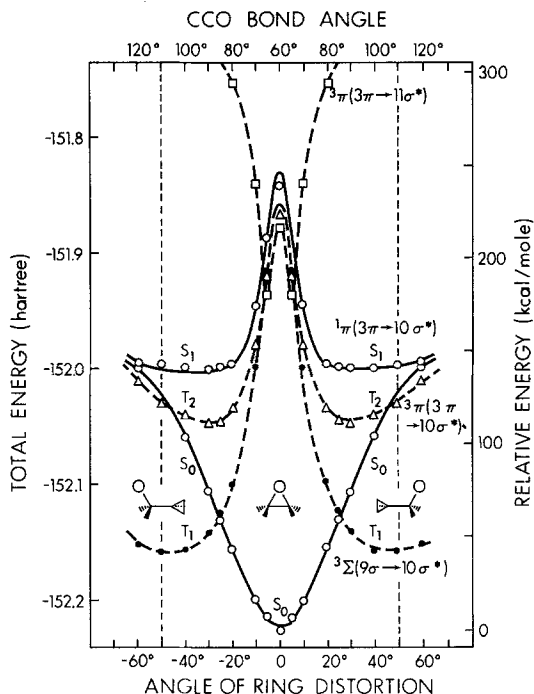| State	Basis set A			Basis set B		
	Total energy (Hartree)		Rotational	Total energy (Hartree)		Rotational
	IV ($\theta = 0°$)	IV' ($\theta = 90°$)	barrier (kcal mol^{-1})	IV ($\theta = 0°$)	IV' ($\theta = 90°$)	barrier (kcal mol^{-1})
S_0	− 152.06694	− 151.96077	+ 66.64	− 152.72062	− 152.66819	+ 32.91
S_1	− 152.00245	− 151.94701	+ 34.80	− 152.62322	− 152.62961	− 4.01
T_1	− 152.15803	− 152.17300	− 9.40	− 152.72643	− 152.64037	+ 54.02
S_2	− 151.84122	− 151.81341	− 17.46	− 152.50355	− 152.56729	− 40.01
T_2	− 152.04607	− 151.99200	+ 30.55	− 152.64129	− 152.56949	+ 45.07
S_3	− 151.75433	− 151.75691	− 1.62	− 152.48855	− 152.54962	− 38.33
T_3	− 151.89501	− 151.84996	+ 28.28	− 152.53616	− 152.56061	− 15.35
S_4	− 151.56903	− 151.68375	− 72.01	− 152.42874	− 152.53017	− 63.67
T_4	− 151.77450	− 151.72330	+ 32.14	− 152.44088	− 152.53404	− 58.48

Fig. 2. Calculated total energy variation as a function of CCO angle (α) for the ground and low lying excited states of ethylene oxide using the non-empirical SCFMO method with minimal basis set A

excited state is also in disagreement with experimental observations: the effect of temperature on the stereochemical behavior of the $O(^3P)$ + olefin systems [12–17] seems to suggest the existence of a small positive barrier for rotation, contrary to the EHMO results illustrated in Fig. 1.

The prediction of the CNDO method with regard to $E(\alpha)$ is qualitatively acceptable but $E(\theta)$ is again negative.

The INDO calculations appear to give qualitatively correct potential energy functions.

Considering the results of the non-empirical calculations, the case of the minimal basis set (A) is of interest for economic reasons and the case of the double zeta basis set (B) from the standpoint of accuracy. The ring distortion potential, $E = E(\alpha)$, was computed with both basis sets and the results are tabulated in Table 7 and illustrated in Figs. 2 and 3. Inspection of these figures reveals that there is a semi-quantitative agreement for the low lying states between the minimal (A) and the double zeta (B) basis set calculations. The results on the torsional potential calculations, $E = E(\theta)$, are presented in Table 8. The computed torsional potentials corresponding to the S_0 and T_1 states are depicted in Fig. 4. Here the two basis sets lead to divergent results, basis set A gives a small negative value for the T_1 potential energy barrier while basis set B gives a substantial positive value. Since minimal basis sets tend to over-emphasize charge distributions
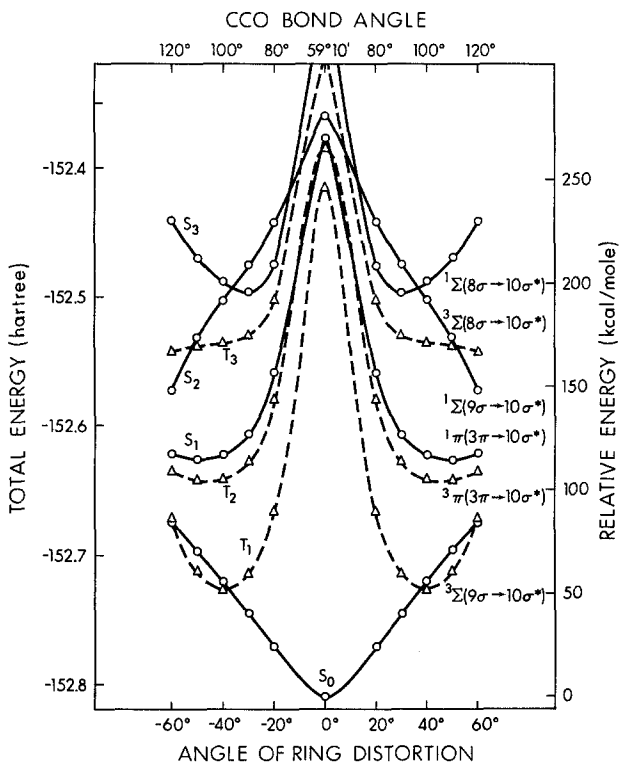
P. Mezey *et al.*

Fig. 3. Calculated total energy variation as a function of CCO angle (α) for the ground and low lying excited states of ethylene oxide using the non-empirical SCFMO method with large basis set B
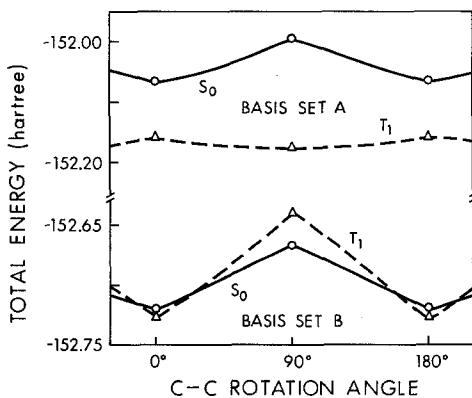

Fig. 4. Calculated total energy variation with two different basis sets, as a function of CC rotational angle (θ) for the ground (S_0) and lowest triplet (T_1) states of ethylene oxide at a CCO angle of $100°$

Table 9. Calculated energies for ring distortion (ΔH_1) and rotational barrier (ΔH_2) at the distorted ring geometry of ethylene oxide

| Method	ΔH_1	ΔH_2	$(\Delta H_1 + \Delta H_2)$[a]
	kcal/mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
Semi-empirical MO			
EHMO	52.3	-1.0	51.3
CNDO	193.5	-4.8	188.8
INDO	160.6	4.0	164.6
Non-empirical MO			
Basis Set A	43.2	-9.4	33.8
Basis Set B	53.2	54.0	107.2

[a] $(\Delta H_1 + \Delta H_2)_{exp} = 52.0$ kcal mol^{-1}. Reference [18].

Table 10. Values of the enthalpy change (ΔH) for the $O(^3P)$ + ethylene reaction calculated by different basis sets

Basis	Total energy (Hartree)			ΔH(kcal mol^{-1})[a]
	Ethylene	$O(^3P)$	Ethylene oxide	
A	-77.66533	-74.66774	-152.22688	$+66.66$
B	-78.01172	-74.79884	-152.81111	-0.35

[a] $\Delta H = H[\triangle] - \{H[> = <] + H[O(^3P)]\}$. $\Delta H_{exp} = -84.13$ kcal mol^{-1}.

and separations, the calculations predict an eclipsed conformation stabilized by long range hydrogen-oxygen interactions:
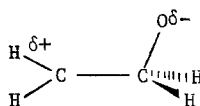
The enthalpy changes of the processes outlined in Scheme 1 were also calculated and the values are compiled in Tables 9 and 10. Here the result with the large basis set calculation is closer to the experimental value although still a considerable discrepancy between computed and experimental values appear.

While from the present computations some insight has been obtained into the potential energy surfaces of the lowest lying electronic states of the ethylene oxide molecule, configuration interaction calculations will be needed for a more quantitative understanding. Further studies along this line are in progress.

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