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A Self Consistent Field Molecular Orbital Treatment, Including Excited States of Cyclopropane, Ethylene Oxide and Ethylenimine

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The electronic structure of cyclopropane, ethylene oxide and ethylenimine, have been investigated using the Pople-Segal Complete Neglect of Differential Overlap self consistent field molecular orbital method, including all valence electrons. The theory gives a good account of the ground state charge distributions and dipole moments and a reasonable interpretation of the electronic spectra of the three molecules.

Die Elektronenstruktur von Cyclopropan, Äthylenoxid und Äthylenimin wurde mit Hilfe der Pople-Segal CNDO-SCF-MO Methode untersucht. Die Theorie gibt gute Ergebnisse für die Ladungsverteilungen im Grundzustand, für die Dipolmomente und für eine Interpretation der Elektronenspektren.

Les structures électroniques du cyclopropane, de l'oxyde d'éthylène et de l'éthylèneimine, ont été étudiées en utilisant la méthode S.C.F. de Pople-Segal comportant tous les électrons de valence et négligeant totalement le recouvrement différentiel. La théorie rend bien compte des distributions de charge et des moments dipolaires de l'état fondamental et donne une interprétation raisonnable des spectres électroniques des trois molécules.

Introduction

The ground state electronic structures of cyclopropane [3, 6, 7, 29, 31, 33] and ethylene oxide [3, 20, 25, 33] have received a considerable amount of attention. Ethylenimine [3] on the other hand has been comparatively neglected. Early qualitative descriptions with assumed hybridization schemes for the atoms concerned [20, 25, 31], have been superceded in recent years by more quantitative models. All three molecules have been discussed using the maximum total overlap criterion [3, 6, 7, 29]. The latter provides a basis for determining a suitable set of hybridized bonding orbitals which is intuitively appealing but without a satisfactory theoretical basis. For cycloalkanes the method gives reasonable results, but for heterocyclic molecules some arbitrary assumptions [3, 6, 7, 29] have to be made for non-bonding orbitals, and this is clearly unsatisfactory. More recently cyclopropane has been the subject of two self consistent field molecular orbital calculations [1, 8]. Dewar and Klopman's calculation [8] is the most sophisticated yet carried out on cyclopropane and successfully reproduces the heat of formation. Brown and Krishna [1] have used a modified Pariser-Parr-Pople SCF MO method to discuss the excited states of cyclopropane. The carbon atoms were assumed to be sp^2 hybridized and the hydrogen atoms were not explicitly taken into account. The results for the excited states were not in particularly good agreement with experiment. There appears to have been no previous calculations on the excited states of ethylene oxide and ethylenimine. In the light of this discussion a self consistent field molecular orbital calculation on the ground states of cyclopropane, ethylene oxide and ethylenimine is clearly worthwhile.

Method of Calculation

The calculations have been carried out using the Pople-Segal Complete Neglect of Differential Overlap Method II [22, 23, 24]. The theory has been applied to the calculation of ground state properties for numerous small molecules with a good deal of success and recently the method has been employed to investigate the excited states of benzene [5] and furan [4]. The elements of the F matrix are given by Eqs. (1) and (2) (notation Ref. [24]).

$$F_{\mu\mu} = U_{\mu\mu} + \left(P_{AA} - \frac{1}{2} P_{\mu\mu}\right)\gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB} \tag{1}$$

where

$$U_{\mu\mu} = -I_\mu - (Z_A - 1)\gamma_{AA}$$

$$F_{\mu\nu} = \beta - \frac{1}{2} P_{\mu\nu}\gamma_{AB}\,. \tag{2}$$

Eq. (1) neglects the penetration terms, the equations are formally similar to those used in the highly successful Pariser-Parr-Pople SCF theory.

As in the latter theory, the main problem is the estimation of the core and repulsion integrals and the β's which occur in the off diagonal elements of the F matrix. Pople and co-workers [23, 24] have estimated the one centre core integrals from the average of valence state ionization potentials and electron affinities, however valence state ionization potentials are in general more accurately known than electron affinities, so we have approximated the core integrals as the average of valence state ionization potentials in the manner described by Sichel and Whitehead [26].

In their original papers Pople and Segal [23, 24] assigned to γ_{AA} the analytic value of the electrostatic repulsion energy of two electrons in a slater s orbital. This does not allow for correlation energy, and hence we prefer to use the method due to Pariser [19], which has been applied so successfully in the PPP SCF method of evaluating the γ_{AA} from Eq. (3).

$$\gamma_{AA} = I_{AA} - A_{AA} \tag{3}$$

where I_{AA} is the valence state ionization potential of atom A and A_{AA} is the valence state electron affinity of atom A. Sichel and Whitehead [26] have investigated this method in detail and the parameters used here are taken from their paper.

The two centre repulsion integrals γ_{AB} were calculated from the corresponding one centre repulsion integrals using the refined Mataga procedure [15, 18] Eq. (4).

$$\gamma_{AB} = \frac{14.397}{(a_{AB}^2 + r_{AB}^2)^{\frac{1}{2}}} \quad \text{where} \quad a_{AB} = \frac{(2 \cdot 14.397)}{\gamma_{AA} + \gamma_{BB}}\,. \tag{4}$$

The first term in the off diagonal elements of the F matrix (β's) were made proportional to overlap integrals in the original Pople papers [23, 24], in order to maintain the invariance to the transformation of atomic orbital basis functions. The required overlap integrals were calculated using Slater orbitals and orbital exponents calculated using Slater's rules, except for the hydrogen 1 *s* orbital (*Z* effective taken as 1.2). However Burns [2] has recently shown that Slater orbitals defined using Slater's rules, are not good approximations to SCF orbitals at distances from the nuclei appropriate for bonding and has devised a modified set of Slater's rules. The orbitals defined in this manner yield overlap integrals which approximate those calculated using SCF orbitals, in particular the slow tailing off of the latter is reproduced. In general overlaps calculated in this manner are larger than those obtained using Slater's rules, and we have preferred to use them in this work. In crude pictorial terms $\beta_{\mu\nu}$ represents the energy of the overlap density $S_{\mu\nu}$ in the average field of the two cores μ and ν. The direct proportionality of β to overlap integral is therefore quite a drastic approximation. In their treatment of benzene Clark and Ragle [5] found it necessary to reduce Poples proportionality constants by approximately half for carbon. We prefer instead to use another empirical relationship Eq. (3) due to Mulliken, Wolfsberg and Helmholtz [32].

$$\beta_{\mu\nu} = \frac{K(I_{\mu\mu} + I_{\nu\nu})}{2} S_{\mu\nu} \tag{5}$$

where $I_{\mu\mu}$ and $I_{\nu\nu}$ are appropriate valence state ionization potentials of atoms μ and ν. K is a constant and $S_{\mu\nu}$ is the overlap integral between atoms μ and ν. The use of Eq. (3) is open to criticism on the grounds that it is not invariant to a transformation of atomic orbital basis functions. However, preliminary calculations showed that this effect is negligible compared with the total energy calculated for the molecule.

The parameter K was adjusted to give a good overall fit to the electronic spectra of cyclopropane and ethylene oxide. A value $K = 0.78$ was found to be appropriate.

Table 1

Orbital	Atom	Z effective	$-I_{\mu\mu}$	$-U_{\mu\mu}$	$\gamma_{\mu\mu}$
1*s*	H	1.2	13.60	13.60	12.85
2*s*	C	3.150	20.07	50.69	10.207
2*p*	C	2.800	10.91	41.53	
2*s*	N	3.750	25.89	70.09	11.05
2*p*	N	3.300	13.65	57.85	
2*s*	O	4.400	33.18	101.31	13.625
2*p*	O	3.950	16.16	84.28	

Table 1 lists the parameters employed in these calculations. Bond lengths and angles were taken from Ref. [27], the co-ordinate and numbering systems are shown in Fig. 1.

The calculations were carried out on the University of Newcastle's KDF 9 computer using a program kindly supplied by Drs. D. R. Armstrong and P. G. Perkins. Configuration interaction between all singly excited states involving the four lowest unoccupied and four highest occupied orbitals has been included. Initial matrices were calculated using a separate program and used as input data, together with atomic co-ordinates, gammas and core charges. Overlap integrals were calculated from a compilation of master formulae kindly supplied by Dr. P. G. Perkins.

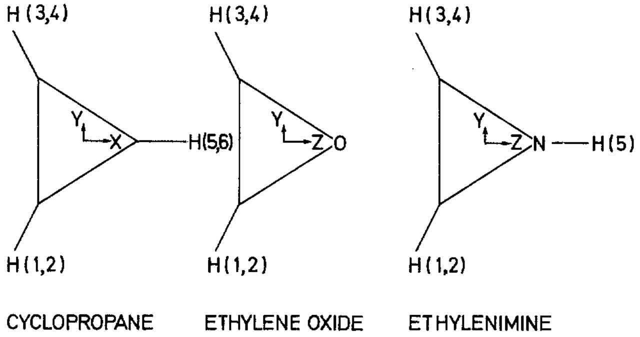

Fig. 1. Numbering and co-ordinate systems for cyclopropane, ethylene oxide and ethylenimine (H_5 is cis to H_2 and H_4 in ethylenimine)

Results and Discussion

1. Electron Distribution and Dipole Moments

Table 2 shows the calculated charge distribution for cyclopropane, ethylene oxide and ethylene imine.

Table 2. *Calculated charge distribution for cyclopropane, ethylene, oxide and ethylenimine*

Compound	Atom	Electron population	δ (charge)
Cyclopropane	H_1, H_6	0.97336	+0.02664
	C_1, C_3	4.05328	−0.05328
Ethyline oxide	H_1, H_4	0.97240	+0.02760
	C_1, C_2	3.85115	+0.14885
	O	6.40809	−0.40809
Ethylenimine	H_1, H_3	0.96855	+0.03145
	H_2, H_4	0.98363	+0.01637
	H_5	0.82183	+0.17817
	C_1, C_2	3.91305	+0.08695
	N	5.44770	−0.44770

The hydrogen atoms in cyclopropane and ethylene oxide carry a small positive charge as do (H_1, H_3) and (H_2, H_4) in ethylenimine. The hydrogen attached to nitrogen in ethylenimine has an appreciable positive charge. The charge on the carbon atoms reflect the inductive order $O > N > C$, the charge being small and negative for cyclopropane and small and positive for ethylene oxide. The nitrogen and oxygen atoms both carry appreciable negative charges.

The overall charge distribution in a molecule is reflected in some measure by the total dipole moment. The major contributions to the dipole moments of the three molecules are from: a) the net atomic charge densities, b) the atomic (*sp*) polarizations resulting from mixing of *s* and *p* orbitals on each atom. The dipole moment of cyclopropane is zero by symmetry, the contributions (a) and (b) and total dipole moments for ethylene oxide and ethylenimine are shown in Table 3. A negative dipole moment is defined in the sense $\mathrm{O} \leftarrow\!\!\!+ \mathrm{C_2H_4}$, $\mathrm{H{-}N} \leftarrow\!\!\!+ \mathrm{C_2H_4}$, for ethylenimine the vector is directed towards the lone pair on nitrogen at 43° 27′ to the plane of the ring. The calculated dipole moments calculated in Table 3 are in good agreement with the experimentally determined values.

Table 3. *Calculated contributions to the dipole moments of ethylene oxide and ethylenimine (debyes)*

	Contribution from						Total	Experimental [16]
	(a)			(b)				
	x	y	z	x	y	z		
Ethylene oxide	−1.36	0	0	−0.36	0	0	−1.72	−1.90
Ethylenimine	−0.78	0	−0.35	−0.34	0	−0.72	−1.55	−1.89

2. *Eigenvalues*

Table 4 shows the calculated eigenvalues for cyclopropane, ethylene oxide and ethylenimine. Applying Koopman's theorem, the calculated ionization potentials are cyclopropane 11.283 eV, ethylene oxide 11.603 eV, ethylenimine 11.137 eV; the experimental values are 10.06 eV [14], 10.57 eV [14], and 9.94 eV [9]. The calculated values are higher than the experimental values as is usual with this type of calculation, but differences are well reproduced. The B_1 orbital at −12.293 eV in ethylene oxide is largely localized on oxygen with a large contribution from the $2p\underline{z}$ orbital. The A' and A'' orbitals at 12.477 eV in ethylene imine have large contributions from orbitals on nitrogen.

Table 4

Cyclopropane		Ethylene oxide		Ethylenimine	
A'_1	−40.481	A_1	−42.897	A'	−41.923
E'	−25.236	A_1	−27.538	A'	−26.301
E'	−25.236	B_2	−25.425	A''	−25.440
A''_2	−20.988	B_1	−20.465	A'	−20.822
A'_1	−14.971	A_1	−14.993	A'	−15.163
E''	−13.448	A_2	−13.885	A''	−13.703
E''	−13.448	B_2	−13.428	A''	−12.477
E'	−11.283	B_1	−12.293	A'	−12.477
E'	−11.283	A_1	−11.603	A'	−11.137
A'_2	2.616	B_2	2.024	A''	2.266
E'	3.451	A_1	2.966	A'	3.284
E'	3.451	B_2	3.170	A''	3.344
A''_2	4.201	B_1	4.355	A'	4.382
A'_1	4.535	A_1	4.546	A'	4.614
E'	4.994	B_2	4.657	A''	4.812
E'	4.994	A_2	5.196	A''	5.406
E''	5.555			A'	5.499
E''	5.555				

3. Electronic Spectra

Cyclopropane and ethylene oxide both show strong absorption in the vacuum ultra violet [11, 12, 13, 14, 30]. The complexity of the overlapping band systems makes it virtually impossible however to assign electronic transitions with any degree of certainty. The most that can be hoped for at the present time is a general picture of the absorption spectra of these molecules. The electronic spectrum of ethylenimine does not appear to have been investigated previously.

a) Cyclopropane. Table 5 shows the calculated and observed excited states of cyclopropane.

Table 5. *Calculated and observed excited states of cyclopropane (in eV)*

Singlet	Calculated Oscillator Strength	Triplet	Observed [26]
A'_2 6.677	0	E' 5.952	
E' 6.927	0.041	A'_2 6.677	6.79
A'_1 7.770	0	E' 7.192	7.78
E' 8.460	1.10	A'_1 7.656	8.55
E'' 8.475	0	E'' 8.383	
E'' 8.786	0	E'' 8.771	
A''_2 9.716	0.44		10.32

The electronic spectrum of cyclopropane has been investigated experimentally by Wagner and Duncan [30]. The longest wavelength absorption centred around 6.79 eV has an extinction coefficient [17] of ~10 and consists of twelve bands. The calculation of Brown and Krishna [1] suggests that this absorption is due to a singlet-triplet transition. However the extinction coefficient is rather high for this to be an acceptable explanation. The calculation here suggests that this absorption is due to the symmetry allowed, degenerate ${}^1E' \leftarrow {}^1A'$ transition, which is polarized in the plane of the molecule. The observed transitions at 7.78 eV, 8.55 eV, and 10.32 eV are much more intense than the band at 6.79 eV.

The strong transitions at 8.55 eV and 10.32 eV may be assigned to the ${}^1E' \leftarrow {}^1A'$ transitions at 8.460 eV and the ${}^1A''_2 \leftarrow {}^1A'$ transition at 9.716 eV respectively. The latter is polarized perpendicular to the molecular plane and arises from an excitation mainly involving orbitals between the carbon and hydrogen atoms, as do the symmetry forbidden ${}^1E'' \leftarrow {}^1A'$ transitions. There remains the transition observed at 7.78 eV. A possible interpretation is that the ${}^1A'_1 \leftarrow {}^1A'_1$ transition becomes vibronically allowed. A vibration which offers a large perturbation is the ring deformation frequency ν_{11} [10] symmetry E'. Intensity could then be *borrowed* from the ${}^1E' \leftarrow {}^1A'_1$ transition which is very similar in energy.

b) Ethylene Oxide. Table 6 shows the calculated and observed excited states of ethylene oxide.

The region from 2120–1660 Å (5.83 eV–7.47 eV) consists of a continuum with two or three overlapping diffuse bands starting at 1715 Å (7.23 eV) [12, 13, 14]. The latter has been assigned to an $N-V$ [12, 13, 14] transition ($B \leftarrow X$) which corresponds to the calculated ${}^1B_2 \leftarrow {}'A_1$ transition at 6.992 eV. This is polarized in the plane of the molecule perpendicular to the C_2 axis. The ${}^1B_1 \leftarrow {}^1A_1$

transition predicted at 6.342 eV is polarized at right angles to the plane of the molecule and results from excitation of an electron in an orbital largely centred on the oxygen to an orbital with considerable C–H antibonding character and could reasonably be described as a $\sigma^* \leftarrow n$ transition. In dimethyl ether the corresponding transition occurs at ~6.75 eV. A value of 6.342 eV for ethylene oxide would thus appear to be quite reasonable. A second somewhat sharper band system starts at 1572 Å [12, 13, 14], it is also overlapped by a continuum. This transition may be assigned to the ${}^1B_1 \leftarrow {}^1A_1$ transitions at 8.390 eV. The $D \leftarrow X$, $E \leftarrow X$ and $F \leftarrow X$ transitions at 8.64 eV, 8.96 eV and 9.56 eV can then be assigned to the ${}^1B_2 \leftarrow {}^1A_1$ (8.490 eV) ${}^1A_1 \leftarrow {}^1A_1$ (8.675 eV) and ${}^1A_1 \leftarrow {}'A_1$ (9.389 eV) transitions respectively in satisfactory agreement with experiment.

Table 6. *Calculated and observed excited states of ethylene oxide (in eV)*

Singlet	Calculated Oscillator Strength	Triplet	Observed (notation Ref. [12])	
A_2 5.607	0	B_2 5.163		
B_2 6.296	0.064	A_2 5.589	5.83–7.23	$A \leftarrow X$
B_1 6.342	0.033	B_1 6.190		
A_1 6.528	0.001	A_1 6.290		
B_2 6.992	0.048	B_2 6.760	7.23	$B \leftarrow X$
A_2 8.271	0	A_1 6.814		
B_1 8.389	0.001	B_2 7.630	7.89	$C \leftarrow X$
B_1 8.397	0.011	A_2 8.094		
B_2 8.490	0.430	B_1 8.347	8.64	$D \leftarrow X$
A_1 8.675	0.120	B_1 8.390	8.96	$E \leftarrow X$
A_1 9.389	0.048		9.56	$F \leftarrow X$

c) Ethylenimine. The electronic spectrum of ethylenimine does not appear to have been measured, however comparison may be drawn with the electronic spectra of simple aliphatic amines such as methylamine and dimethylamine and a cyclic compound such as pyrrolidine.

Table 7. *Calculated excited states of ethylenimine (in eV)*

Singlets	Calculated Oscillator strength (f)	Triplet	CH_3NH_2 [28]	f	$(CH_3)_2NH$ [28]	f	C_4H_9N [21]	f
A'' 5.982	0.042	A'' 5.222	5.77	0.017	5.58	0.0017	5.32	0.05
A' 6.503	0.010	A' 6.267	7.13	0.084	6.510	0.10	7.25	0.08
A'' 6.814	0.012	A'' 6.621						
A'' 7.220	0.030	A' 6.698						
A' 7.870	0.043	A'' 6.924						
A' 8.186	0.020	A'' 7.653						
A'' 8.305	0.167	A' 7.767						
A' 8.367	0.101	A' 8.197						
A' 8.595	0.005	A' 8.580						
A' 9.070	0.293	A'' 8.592						
A'' 9.206	0.337	A' 8.593						

Table 7 shows the calculated excited states of ethylenimine and the two longest wavelength transitions for the representative compounds.

The calculated transition energies and oscillator strengths for the first two transitions of ethylenimine would seem to be reasonable.

References

1. Brown, R. D., and V. G. Krishna: J. chem. Physics **45**, 1482 (1966).
2. Burns, G.: J. chem. Physics **41**, 1521 (1964).
3. Certain, P. R., V. S. Watts, and J. H. Goldstein: Theoret. chim. Acta (Berl.) **2**, 324 (1964).
4. Clark, D. T.: Submitted for publication in J. chem. Soc. (London).
5. —, and J. L. Ragle: J. chem. Physics **46**, 4235 (1967).
6. Coulson, C. A., and W. E. Moffitt: Philos. Mag. **40**, 1 (1949).
7. —, and T. H. Goodwin: J. chem. Soc. (London) **1963**, 3161.
8. Dewar, M. J. S., and G. Klapman: J. Amer. chem. Soc. **89**, 3089 (1967).
9. Gallegos, E. J., and R. W. Kiser: J. physic. Chem. **65**, 1177 (1961).
10. Herzberg, G.: Infrared and Raman spectra of polyatomic molecules, p. 352. New York: D. Van Nostrand Co. Inc. 1945.
11. — Electronic spectra and electronicstructure of polyatomic molecules, p. 544, 642. New York: D. Van Nostrand Co. Inc. 1966.
12. — Electronic spectra and electronic structure of polyatomic molecules, p. 548, 651. New York: D. Van Nostrand Co. Inc. 1966.
13. Lin, T. K., and A. B. F. Duncan: J. chem. Physics **17**, 241 (1949).
14. Lawrey, A., and K. Watanabe: J. chem. Physics **28**, 208 (1958).
15. Mataga, N., and K. Nishimoto: Z. physik. Chem. (Frankfurt) **13**, 140 (1957).
16. McClellan, A. L.: Tables of experimental dipole moments. San Francisco: W. H. Freeman and Co. 1963.
17. Muel, B., and M. Kasha: Quoted in Ref. [1].
18. Ohno, K.: Theoret. chim. Acta (Berl.) **2**, 219 (1964).
19. Pariser, R.: J. chem. Physics **21**, 568 (1953).
20. Parker, R. E., and N. S. Isaacs: Chem. Reviews **59**, 737 (1959) and references therein.
21. Pickett, L. W., and M. E. Corning: J. Amer. chem. Soc. **75**, 1618 (1953).
22. Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, 5129 (1965).
23. —, and G. A. Segal: J. chem. Physics **43**, 5136 (1965).
24. — — J. chem. Physics **44**, 3289 (1966).
25. Rosonsky, A.: The chemistry of heterocyclic coumpounds, Editor A. Wensberger. Heterocyclic compounds with 3 and 4 membered rings, part 1, page 1. New York: Interscience Publishers 1964.
26. Sichel, J. M., and M. A. Whitehead: Theoret. chim. Acta (Berl.) **7**, 32 (1967).
27. Sutton, L. E. (Editor): Interatomic distances. London: The Chemical Society 1958.
28. Tannenbaum, E., E. M. Coffin, and A. J. Harrison: J. chem. Physics **21**, 311 (1953).
29. Veillard, A., and G. Del Re: Theoret. chim. Acta (Berl.) **2**, 55 (1964).
30. Wagner, P., and A. B. F. Duncan: J. chem. Physics **21**, 516 (1953).
31. Walsh, A. D.: Nature **159**, 165, 712 (1947).
32. Wolfsberg, M., and L. Helmholtz: J. chem. Physics **20**, 837 (1952).
33. Yonezawa, T., I. Morishima, M. Fuzü, and K. Fukui: Bull. chem. Soc. Japan **38**, 1224 (1965).

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