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### Publication Date

1961-09-01

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UNIVERSITY OF CALIFORNIA  
Lawrence Radiation Laboratory  
Berkeley, California  
Contract No. W-7405-eng-48

SIMPLE MOLECULAR ORBITAL THEORY  
OF THE DICHLOROETHYLENES\*

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Simple Molecular Orbital Theory  
of the Dichloroethylenes\*

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ABSTRACT

A simple molecular orbital treatment, including overlap, has been employed to compute the electron distribution and energy eigenvalues of the dichloroethylenes. The coulomb and exchange integrals used were those previously employed for vinyl chloride and were not subject to further adjustment in the present calculations. Comparison with available photoionization potentials, electric dipole moments, and nuclear quadrupole data show, on the whole, a satisfactory agreement between observed and calculated properties. The results obtained are considered to provide support for the occurrence of lone-pair conjugation in the vinyl halides.

\* Financial support of the machine calculations reported herein was provided by the U.S. Atomic Energy Commission in conjunction with The Lawrence Radiation Laboratory.

## INTRODUCTION

The idea that conjugated systems can be viewed in terms of resonance between two or more participating structures has formed the basis for a widely used and often successful method for the rationalization of molecular properties. Recently, however, Dewar and Schmeising<sup>1</sup> have taken the position that resonance effects are relatively unimportant in the ground states of those organic molecules for which only a single classical structure can be written, and that effects usually ascribed to resonance in such cases are in reality to be accounted for primarily by changes in the state of hybridization of the carbon atoms. This viewpoint has been discussed by other authors<sup>2,3</sup> who have reviewed a variety of evidence which appears to indicate that hybridization alone is unlikely to be the sole factor responsible for the characteristic properties of conjugated systems.

The haloethylenes comprise a class of molecules which have long been cited as examples of systems whose properties are significantly affected by resonance.<sup>4</sup> In vinyl chloride, for example, an early estimate of ~ 20% double-bond character ( $\overset{+}{\text{C}}\text{H}_2-\overset{-}{\text{C}}\text{H}-\overset{+}{\text{Cl}}$ ) was inferred from the shortening of the C-Cl bond based upon electron diffraction studies. Further support for the existence of conjugation in the vinyl halides (Cl, Br, I) has been provided by theoretical analyses of the hyperfine structure in the microwave spectra of these molecules, which has its origin in the interaction of the nuclear electric quadrupole with a non-vanishing electric field gradient in the immediate vicinity of the nucleus.<sup>5</sup> This treatment is based upon the formulation of a measure,  $\delta$ , of charge transferred from the halogen atom to the  $\pi$ -electron system, which is to a very good approximation independent of the  $\pi$ -electron system, and which can be expressed in terms of the experimentally determined quadrupole coupling constants. Although the existence of a non-zero value of

$\delta$  in the vinyl halides is to be interpreted as supporting the idea of lone-pair conjugation in these molecules, the actual results indicate that extent of double-bonding is  $\sim 5\%$ , which is considerably smaller than the value of  $20\%$  previously reported.

In the subsequent development of this approach, it was shown that the quantity,  $\delta$ , could be used to determine empirically the value of the carbon-halogen exchange integral,  $\beta_{cx}$ , in the simple molecular orbital (MO) treatment of the  $\pi$ -electron systems of the vinyl halides.<sup>6</sup> Moreover, without further adjustment of any of the parameters involved, the results of this MO treatment were found to predict other molecular properties of several vinyl and phenyl halides in rather good agreement with observation.<sup>7,8</sup>

It is the purpose of this paper to present the results of similar calculations for the three dichloroethylenes. The MO parameters employed have been slightly altered to reflect the improved values of the internuclear distances presently available for vinyl chloride. Apart from these minor changes, all the calculations were carried out without adjustment of the parameters chosen at the outset.

## THEORY

The LCAO-MO calculations, with inclusion of overlap, requires that we solve the simultaneous matrix equations

$$\tilde{T} \tilde{H} \tilde{T} = \tilde{H}^0 \quad (1)$$

$$\tilde{T} \tilde{S} \tilde{T} = \tilde{I} \quad (2)$$

where  $\tilde{H}$  is the Hamiltonian in the AO basis,  $\tilde{S}$  is the overlap matrix in the same basis,  $\tilde{H}^0$  is a diagonal matrix, and  $\tilde{I}$  is the unit matrix. These equations may be rewritten in a form suitable for solution by high speed digital computers as

$$\tilde{C} \tilde{S}^{-1/2} \tilde{H} \tilde{S}^{-1/2} \tilde{C} = \tilde{H}^0 \quad (3)$$

$$\tilde{C} \tilde{C} = \tilde{I} \quad (4)$$

$\tilde{S}^{-1/2}$  is readily obtained from a series expansion in powers of  $\tilde{\epsilon}$  where  $\tilde{\epsilon} = \tilde{S} - \tilde{I}$ . The one electron MO's are given by

$$\tilde{\Psi} = \tilde{C} \tilde{S}^{-1/2} \phi \quad (5)$$

We next define an electron density matrix,  $\tilde{n}^0$ , which describes the distribution of electrons among the various one-electron eigenfunctions,  $\tilde{\Psi}$ . In the MO basis  $\tilde{n}^0$  is diagonal and  $n_{11}^0$  is the number of electrons in the state  $\tilde{\Psi}_1$ . With this definition, the molecular expectation value,  $\bar{A}$ , of an operator  $A_{op}$  is given by the equation

$$\bar{A} = \text{Tr} \tilde{n}^0 \tilde{A}^0 \quad (6)$$

where  $\tilde{A}^0$  is the matrix representative of  $A_{op}$  in the MO basis. Transformation of this expression to the AO basis gives:

$$\bar{A} = \text{Tr} \tilde{n} \tilde{A} \quad (7)$$

$$\tilde{n} = \tilde{S}^{-1/2} \tilde{C} \tilde{n}^0 \tilde{C} \tilde{S}^{-1/2} \quad (8)$$

Having briefly described the computational method, we now proceed to apply it to the  $\pi$  electron systems in the dichloroethylenes. A total of six electrons



must be considered and the AO basis consists of a 2p AO centered on each of the carbon atoms and a 3p AO centered on each of the chlorine atoms. The next steps in the procedure are the evaluation of the matrix  $S$ , and the choice of suitable values for the elements of  $H$ .

Evaluation of  $\tilde{H}$  and  $\tilde{S}$

Values of the required structural parameters were taken as  $d(C-C) = 1.333$ ,  $d(C-Cl) = 1.724$  A, and  $\angle C-C-Cl = 123.6^\circ$ ; these values are based on recent microwave studies of  $CH_2CHCl$ <sup>9</sup> and  $CH_2CCl_2$ .<sup>10</sup> Using these values,  $S_{C-C} = 0.273$  and  $S_{C-Cl} = 0.137$  were obtained from published tables for overlap integrals of Slater functions.<sup>11</sup> Values of  $S_{Cl-Cl}$  were found to be more than a factor of ten smaller. Accordingly both  $S_{Cl-Cl}$  and  $H_{Cl-Cl}$  were set equal to zero.

As recommended by Mulliken,<sup>12</sup> the value of the carbon coulomb integral was taken as  $H_C = -8.14$  ev;  $H_{C-C}$  was chosen as  $-5.23$  ev so as to reproduce the observed ionization potential of ethylene when used with the  $S_{C-C}$  value above. The value of the chlorine coulomb integral was fixed by the equation  $H_{Cl} = H_C + (V_{Cl} - V_C) = -10.64$  ev, the  $V$  being appropriate valence state energies.<sup>13</sup>

Since only nearest neighbor interactions will be considered in this work the only remaining quantity to be determined is  $H_{C-Cl}$ . As shown in Reference 6, this value may be fixed by using the observed quadrupole coupling constants of  $CH_2CHCl$ . Since the previously determined value was based on different structural parameters this calculation has been repeated with the results given in Table I. The indicated choice is  $H_{C-Cl} = -2.35$  ev and it may be noted in passing that this value correctly reproduced the observed ionization potential.

This completes the specification of  $\tilde{H}$  and  $\tilde{S}$ . We are now able to perform a simple MO calculation for the dichloroethylenes in which there are no adjustable parameters. All of the computations described here were performed on an IBM 704 computer and were carried to eight significant figures. The series expansion for  $S^{-1/2}$  was carried through the tenth power of  $\xi$ .

### 1,2-Dichloroethylene

The calculated energy levels are given in Table II. Since the nearest neighbor approximation is used here these values, and also the value of  $n_2$ , apply equally well to both the cis and trans species. This calculation therefore predicts that the ionization potentials of the cis and trans species are identical and are equal to  $-E_2$ , i.e., have the value of 9.66 ev. It is interesting to note that although Walsh<sup>14</sup> has reported ionization potential values for the cis and trans species of 9.65 and 9.96 ev, more recent photoionization work by Watanabe, et al.,<sup>15</sup> resulted in the values  $9.65 \pm .01$  and  $9.66 \pm .03$  ev.

Pertinent elements in the AO basis of the ground state density matrix are given in Table III; the AO's are labelled according to the scheme Cl(3)-C(1)-C(2)-Cl(4). The calculated value of the lone pair defect is  $\delta = 2 - n_{33} = .051$ . Unfortunately no precise experimental value of  $\delta$  is available for comparison. However data from the microwave spectrum of cis 1,2-dichloroethylene indicate that  $\delta$  has a probable value in the range .04-.06.<sup>16</sup>

An additional check on the probable validity of the density matrix is afforded by calculating the dipole moment of the  $\pi$  electron system according to the equation  $\mu_{\pi} = e \sum_j Z_j R_j - e \text{Tr } \underline{p} \underline{r}$ ,  $Z_j$  being the charge of the  $j$ th nucleus when stripped of its  $\pi$  electron(s),  $R_j$  the corresponding position vector, and  $\underline{r}$  being the matrix of the electronic position vector. The required elements of  $\underline{r}$  may be calculated in closed form from Slater functions and the molecular geometry. The result is that  $\mu_{\pi}$  is opposite to the expected direction of the  $\sigma$  moment and has a magnitude of 0.60 D.

In order to compare this value with experiment it is necessary to assume independence of the  $\sigma$  and  $\pi$  moments and then to estimate the value of  $\mu_{\sigma}$  from

from the observed moments of suitable saturated molecules. In the present case, in order to reproduce the observed moment of 1.89D,<sup>17</sup> a  $\sigma$  moment of 2.5 D is required. Using the structural parameters previously given this is equivalent to a moment of 1.5D lying along each of the C-Cl bonds. Since Smyth<sup>18</sup> gives the value of the C-Cl bond moment as 1.46D, the calculated value of  $\mu_{\pi}$  is in acceptable agreement with experiment, particularly in view of the simplifications and assumptions introduced.

#### 1,1-Dichloroethylene

The computational technique used for the 1,2-dichloroethylenes may also be applied to the case of 1,1-dichloroethylene. The previously given values for the elements of  $\underline{H}$  and  $\underline{S}$  are appropriate here although the matrices themselves will reflect the fact that the two carbon centers are no longer equivalent. Again, it should be pointed out that there are no adjustable parameters.

The results of the energy level calculations are given in Table II, where they may be compared with those for CHClCHCl. The predicted first ionization potential has the value 9.78 ev. From Rydberg series data Teegan and Price<sup>19</sup> find the value 9.46 ev; there appears to be no photoionization value available. Since it appears unlikely that the ionization potential of  $\text{CH}_2\text{CCl}_2$  is lower than that of CHClCHCl this experimental value is subject to suspicion.

Results of the electron density calculation for the ground electronic state are shown in Table IV; the labelling scheme is given by C(1)-C(2)-Cl(3)-Cl(4). In this case the calculated value of  $S$  is .060. From their study of the microwave spectrum of 1,1-dichloroethylene, Sekino and Nishikawa<sup>10</sup> report the value .058.

As before, the electron density matrix may also be used in calculation of the electric dipole moment arising from the six  $\pi$  electrons. In this way

it is determined that  $\mu_{\text{v}}$  has the magnitude 1.39D and is opposite to the expected direction of the moment resulting from the  $\sigma$  electrons. In this case, because large inductive effects between the two C-Cl bond moments are likely, attempts to assign a  $\sigma$  moment seem unprofitable. However, reference to Table V would indicate that the calculated  $\pi$  moment is substantially in agreement with experiment.

### CONCLUSIONS

The results of the calculations described above indicate that the general approach and the values of the MO parameters employed in the case of vinyl chloride can be successfully transferred to the dichloroethylenes. As far as experimental data are available for comparison, the computed values of  $\delta$ ,  $\mu$ , and  $I$  appear to be in satisfactory agreement with observation. These results further strengthen the contention that appreciable conjugation exists between the lone-pair electrons on a halogen atom and the  $\pi$ -electron system to which it is bonded, and that the effects of this conjugation are evident in at least some of the important molecular properties of the haloethylenes.

**ACKNOWLEDGMENTS**

One of us (J.H.G.) wishes to express his appreciation to the Army Research Office, Durham, for the support of his efforts in this study.

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Table ICH<sub>2</sub>CHCl

<u>-H C-Cl' e.v.</u>	<u>I, e.v.</u>	<u>S</u>
2.30	10.03	.055
2.35	10.00	.061
2.40	9.97	.066
Exptl.	10.00 <sup>a</sup>	.061 <sup>b</sup>

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<sup>a</sup> Ref. 15

<sup>b</sup> Ref. 9

Table II

Calculated MO Energies (ev)

	<u>CHClCHCl</u>	<u>CH<sub>2</sub>CCl<sub>2</sub></u>
-E <sub>1</sub>	3.33	3.29
-E <sub>2</sub>	9.66	9.78
-E <sub>3</sub>	10.79	10.64
-E <sub>4</sub>	11.29	11.35

Table III

Electron Density in  $\text{CHCl}_2\text{CHCl}_2$ 

$n_{11}, n_{22}$	0.826
$n_{33}, n_{44}$	1.949
$n_{12}$	0.768
$n_{13}, n_{24}$	0.056

Table IV

Electron Density in  $\text{CH}_2\text{CCl}_2$ 

$n_{11}$	0.943
$n_{22}$	0.716
$n_{33}, n_{44}$	1.940
$n_{12}$	0.757
$n_{32}, n_{42}$	0.088

Table V

	<u>Observed Moment</u>	<u>Calculated <math>\pi</math> Moment</u>
cis CHClCHCl	1.89 D <sup>a</sup>	0.60 D
CH <sub>2</sub> CCl <sub>2</sub>	1.34 D <sup>b</sup>	1.39 D

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<sup>a</sup> Ref. 17

<sup>b</sup> J.A. Howe and W.H. Flygare, "Strong Field Stark Effect", to be published.