A Molecular Orbital Treatment of cis- and trans-Dichloroethylenes

By Shinhachiro SAITO*

(Received March 15, 1962)

It is well known that, for the 1,3-butadienes, the trans isomer is more stable than the cis isomer. Parr and Mulliken[1] have carried out SCF MO[2] calculations for the π electrons of these molecules, confirming this view theoretically.

Dichloroethylenes are a special case in that the cis isomer has the lower energy. This fact has been investigated by many authors[3] on the basis of thermodynamic or vibrational data. Pitzer and Hollenberg[3] suggested that the anomalous stability of the cis isomer of dichloroethylene is associated with the unlike charges between those on the Cl atom for the cis isomer and for the trans isomer. For *cis*- or *trans*-dichloroethylene, no LCAO SCF treatment such as Parr and Mulliken's has ever been made. In the present paper, LCAO SCF MO calculations of the π electrons in their ground state are undertaken. The double bond characters, the ionization potentials and the energy difference between cis and trans isomers are discussed in comparing the results with experimental data.

Ground State Orbitals and Energy

The internuclear distances and the bond angles of *cis*- and *trans*-dichloroethylenes, based on microwave or electron diffraction data, are given in the literature[4,5]. They are listed in Table I. In these calculations, it has been assumed that the cis and the trans isomer have the same internuclear distances and the same bond angles. The properly-averaged numerical values based upon Table I are as follows: the skeletones Cl–C–C′–Cl′ are planar; Cl–C–C′ and C–C′–Cl′ angles, 122°; C–C′ distances, 1.38 Å; C–Cl and C′–Cl′ distances, 1.69 Å, as is shown on the last line of Table I and in Fig. 1. These values are consistent with the

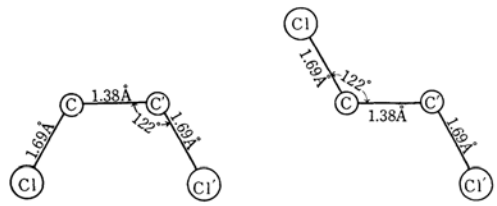
TABLE I. BOND DISTANCES AND BOND ANGLES FOR *cis*- AND *trans*-DICHLOROETHYLENE[a]

Form	Method	d_{C-C} Å	d_{C-Cl} Å	∠C=C–Cl
Cis	(E. D.)*	1.38	1.67	123.5°
	(M. S.)**	1.32	1.70	121°.33′
Trans	(E. D.)	1.38	1.69	122.5°
The adopted values for both forms in this work		1.38	1.69	122.0°

* (E. D.) is abbreviation of the method of electron diffraction.

** (M. S.) is abbreviation of the method of microwave spectra.

a) See Refs. 4 and 5.



Cis form (planar) Trans form (planar)

Fig. 1

experimental data in Table I; also permit us to appropriate the integrals given in the literature[6] to these calculations. Bray and Barnes[7] have shown, in their nulear quadrupole resonance study of multichlorobenzenes, that, in *o*-dichlorobenzene, the out-of-plane bending of the C–Cl bonds causes an increase in the double-bond character. If the same is true for *cis*-dichloroethylene, the ground state orbitals and energy may also be affected by the out-of-plane bending of the C–Cl bond. Therefore, a trial calculation are carried out for a staggered form* (see Fig. 2) of cis isomer at the same time with the planar cis and the trans isomer. The penetration, exchange and hybrid integrals, which are not seen in the literature, have been evaluated by the use of a uniformly-charged sphere model[6,8] and of

* Present address: The Research Institute for Iron, Steel and Other Metals, Tohoku University, Katahira-cho, Sendai.

1) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

2) J. C. C. Roothan, *Rev. Mod. Phys.*, **23**, 69 (1951).

3) R. E. Wood and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 1650 (1941); K. S. Pitzer and J. L. Hollenberg, ibid., **76**, 1493 (1954); Bernstein and Ramsay, *J. Chem. Phys.*, **17**, 556 (1949); Bernstein and Pullin, *Can. J. Chem.*, **30**, 963 (1952).

4) R. Wirel, *Ann. Physik*, **13**, 453 (1932); J. Y. Brockway et al., *J. Am. Chem. Soc.*, **57**, 2693 (1935).

5) T. Shimizu and H. Takuma, *J. Phys. Soc. Japan*, **15**, 646 (1960).

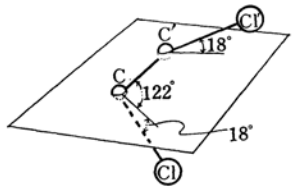
6) M. Simonetta, G. Favini and S. Carra, *Mol. Phys.*, **1**, 181 (1958).

7) P. J. Bray, R. G. Barnes and R. Bersohn, *J. Chem. Phys.*, **25**, 813 (1956).

* In this case, the overlap in the C–Cl bond is evaluated by the following equation (see Ref 7):

$$<\pi_C/\pi_{Cl}>\cos^2 18° + <\pi_C/\pi_{Cl}>\sin^2 18°$$

8) R. Pariser and R. G. Parr, ibid., **21**, 466 (1953).



Cis form (staggered)

Fig. 2

TABLE II

Overlap integrals (dimensionless)

	Cis	Trans	Cis 18°
$S_{CC'}$	0.266	0.266	0.266
S_{CCl}	0.166	0.166	0.182
$S_{CCl'}$	0.022	0.022	—*
$S_{ClCl'}$	0.006	0.000	—*

Penetration integrals (in eV.)

	Cis	Trans
Cl' : CCl = Cl : C'Cl'	0.024	0.043
Cl : CCl' = Cl' : C'Cl	0.015	0.018
C : ClCl' = C' : ClCl	0.001	0.000
Cl' : ClCl' = Cl : ClCl'	0.090	0.005

The symbolism for the integrals adopted here is the same as in the Refs. 1 and 6.

* These values were assumed to be the same as that of cis planer form.

Mulliken's approximation[9]. The overlap integrals are calculated by the equation given by Mulliken et al.[10] Except for the integrals referred to in the literature[1,6], the estimated values of integrals are listed in Table II. Prior to SCF calculations, the starting orbitals were calculated by the simple LCAO MO method. In these calculations, the Coulomb integrals of the chlorine atoms (denoted by α_{Cl}) were evaluated by Coulson's prescription[11], and the resonance integrals between the C and the Cl atom, β_{C-Cl}, were evaluted by Wheland's expression[12]:

$$\alpha_{Cl}-\alpha_C=(X_{Cl}-X_C)\beta_{cc}$$
$$\beta_{C-Cl}=(S_{C-Cl}/S_{cc})\beta_{cc}$$

where X_{Cl} and X_C are the electronegativities of the Cl and the C atoms, and S_{C-Cl} and S_{cc}, the overlap integrals of the C–Cl and C–C' bonds respectively. The molecular orbitals were obtained as follows:

$$\left.\begin{aligned}\phi_1&=0.4024(\chi_{Cl}+\chi_{Cl'})+0.5815(\chi_C+\chi_{C'})\\ \phi_2&=0.6612(\chi_{Cl}-\chi_{Cl'})+0.2506(\chi_C-\chi_{C'})\\ \phi_3&=0.5815(\chi_{Cl}+\chi_{Cl'})-0.4024(\chi_C+\chi_{C'})\\ \phi_4&=0.2506(\chi_{Cl}-\chi_{Cl'})-0.6612(\chi_C-\chi_{C'})\end{aligned}\right\}\quad(1)$$

After eight trials using these orbitals, the four orthonormal SCF orbitals, ψ_i, and the corresponding energy levels, ε_i, were found as follows:

$$\left.\begin{aligned}\psi_1&=\begin{Bmatrix}0.2117\\0.2357\\0.2436\end{Bmatrix}(\chi_{Cl}+\chi_{Cl'})+\begin{Bmatrix}0.5688\\0.5585\\0.5518\end{Bmatrix}(\chi_C+\chi_{C'})\\ \psi_2&=\begin{Bmatrix}0.6636\\0.6614\\0.6575\end{Bmatrix}(\chi_{Cl}-\chi_{Cl'})+\begin{Bmatrix}0.1893\\0.1900\\0.1975\end{Bmatrix}(\chi_C-\chi_{C'})\\ \psi_3&=\begin{Bmatrix}0.6828\\0.6772\\0.6750\end{Bmatrix}(\chi_{Cl}+\chi_{Cl'})-\begin{Bmatrix}0.2876\\0.3072\\0.3224\end{Bmatrix}(\chi_C+\chi_{C'})\\ \psi_4&=\begin{Bmatrix}0.2786\\0.2781\\0.2984\end{Bmatrix}(\chi_{Cl}-\chi_{Cl'})-\begin{Bmatrix}0.8157\\0.8154\\0.8168\end{Bmatrix}(\chi_C-\chi_{C'})\end{aligned}\right\}\quad(2)$$

where the upper value of the coefficients are for the trans-, the middle for planar cis-, and the lower for the staggered cis- form respectively. The orbital energies for the six π-electrons in the field of the core are (in eV.):

ε_1	cis	−18.2491
	trans	−18.5648
	cis(staggered)	−18.5445
ε_2	cis	−12.2857
	trans	−12.0196
	cis(staggered)	−12.3744
ε_3	cis	−10.1897
	trans	− 9.0793
	cis(staggered)	− 9.4966
ε_4	cis	− 6.6847
	trans	− 6.6423
	cis(staggered)	− 7.1360

while the π-electron densities on the chlorine atoms, denoted by q_{Cl}, and the bond order of C–Cl bond, P_{C-Cl}, are:

q_{Cl}	cis	1.9113
	trans	1.9109
	cis(staggered)	1.9032
P_{C-Cl}	cis	0.2854
	trans	0.2860
	cis(staggered)	0.2995

Discussion

In comparing Eqs. 1 and 2, we can see that the results obtained by the simple LCAO MO method agree qualitatively with those resulting from the LCAO SCF calculations.

Although many assumptions are included in the SCF calculations, agreement between the calculated (ε_3) and the experimental (cis: 9.61[13] or 9.66[14]; trans: 9.91[13] or 9.96[14]) values of the ionization potential is fairly good.

As has been shown in the introductory part, the energy of the cis isomer is lower than that

9) R. S. Mulliken, *J. Chim. Phys.*, **46**, 675 (1946).
10) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
11) C. A. Coulson, "Valence", Oxford University Press, London (1952), p. 242.
12) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
13) T. M. Sugden, A. D. Walsh and W. C. Price, *Nature*, **148**, 372 (1941).
14) A. D. Walsh, *Trans. Faraday Soc.*, **41**, 35, 76 (1945).

of the trans isomer. It is generally known that one cannot expect the energy difference between the cis and the trans isomer quantitatively with the results of the ground state energy obtained from the MO treatment mentioned above. However, for a comparison with the experimental data, the energy difference between the cis and the trans isomers is thus estimated from the ground state total π-electron energy, E_n, by the method used by Parr and Mulliken for *cis*- and *trans*-butadienes:

$$E_n \text{ (trans)} - \left\{ \begin{matrix} E_n\text{(cis) or} \\ E_n\text{(cis, staggered)} \end{matrix} \right\} \approx 11 \text{ eV}.$$

This is surprising when compared with experimental data[3], but the calculated sign agrees with the experimetal data in that the cis isomer is more stable than the trans isomer.

The numerical values of the bond order P_{C-Cl} show that the double-bond character in the cis isomer is nearly equal to that of the trans isomer, and that the P_{C-Cl} for the staggered cis form is larger than those of the planar isomers. On the other hand, the nuclear quadrupole coupling constants[15] of the ^{35}Cl atom in the solid cis isomer are smaller than those in the solid trans isomer.

If the ionic character and the *s* character[16] in the chlorine atoms are the same for both molecules, and if the C−Cl bond of the cis isomer is to be staggered from the molecular plane in the solid state, such as in Fig. 2, the difference in the nuclear quadrupole coupling constants of the cis and trans isomers (cis: 70.00 (average), trans: 71.16) may be explained in terms of the difference in the double-bond character of the two molecules.

The author wishes to express his thanks to Dr. Siro Maéda of the Defense Academy, with whom he has been able to discuss this work.

Department of Chemistry
Defense Academy
Yokosuka

15) R. Livingston, *J. Phys. Chem.*, **57**, 496 (1952).
16) C. H. Towns and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).