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The Electronic Structures of *trans* and *cis* Isomers of Some Halogenoethylenes

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By using the closed-shell SCF MO method with the zero-differential overlap approximation for all valence electron systems previously presented by us, the electronic structures of *trans*- and *cis*- substituted ethylenes (treated substituent$=CH_3$, Cl, Br, and I) are studied. The calculated values of the π and valence electron charges, and the total energies of these isomers are presented. The natures of the higher occupied MO's, especially the lone-pair MO's, of chlorinated ethylenes are discussed in connection with the photoelectron observation. The calculated lowest π–π^* singlet transition energies accord well with the observed values. As to the rotational energy changes, the calculated results show that, at the perpendicular configurations, the triplet states for all the treated compounds are lowest, while the intermediate states for the *cis-trans* isomerizations of these compounds may be common to both the isomers.

Many theoretical and experimental studies have been carried out on the electronic structures of *trans*- and *cis*- isomers of substituted ethylenes.[1] On theoretical grounds, semi-quantitative discussions of this problem, however, need to consider explicitly not only the π-electronic structures but also the σ-electronic ones. For example, differences in the electronic structures of these isomers are in some case, mainly dependent on the interactions between the lone pairs of the substituted atoms, and the rotation about the ethylenic CC double bond causes the σ-π mixing. We have already given a semiempirical SCF MO method for all valence electron systems,[2,3] and the electronic structures of *trans*- and *cis*-isomers of butadiene, acrolein, and glyoxal have been calculated in satisfactory agreement with the observed results.[3]

In this paper, the method with an approximation of the zero-differential overlap[4] is used to study the electronic structures of the *trans*- and *cis*-halogenated ethylenes and related compounds, and also those of the twisted configurations caused by the *cis-trans* isomerizations of these compounds. The compounds treated in this paper are as follows: *cis*- and *trans*-butene-2, dichloro-, dibromo-, and diiodoethylenes, and some related chlorinated ethylenes.

Method and Parameters Used

The method employed in this paper is the semiempirical SCF MO method for the closed shell of all valence electron systems, with approximations of the zero-differential overlap and empirical estimation of integral values. In this section, only the used parameters will be described, since the details have been given in previous papers.[4]

The one center exchange integral values and the valence-state ionization potential and electron affinity for the related atoms are estimated from those in Hinze and Jaffe's paper.[5] The values of the orbital exponent are those obtained by Clementi and Raimond.[6] The overlap integrals including the bromine atom

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[1] *E. g.*, P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955); G. M. Wyman, *Chem. Revs.*, **55**, 625 (1955).

[2] T. Yonezawa, K. Yamaguchi, and H. Kato, This Buttetin, **40**, 536 (1967).

[3] H. Kato, H. Konishi, H. Yamabe, and T. Yonezawa, *ibid.*, **40**, 2761 (1967).

[4] T. Yonezawa, H. Konishi, and H. Kato, *ibid.*, **42**, 933 (1969); **41**, 1031 (1968).

[5] J. Hiaze and H. H. Jaffe, *J. Chem. Phys.*, **38**, 1834 (1963).

[6] E. Clementi and D. L. Raimond, *ibid.*, **38**, 2686 (1963).

(the principal quantum number, $n=4$) are calculated by the expansion formulas for $n=5$. The value of the parameter, K, for the estimation of core resonance integrals is taken to be 0.8 for the halogenated ethylenes and for 2-butene.[7] It is estimated so as to reproduce the good accordance between the calculated and observed lowest π–π^* singlet energies in vinyl chloride ($K=0.8$) in stead of in ethylene ($K=0.9$).

The molecular coordinates are adopted from the Sutton's Tables[8] and are summarized in Table 1, where the coordinates of the *cis*-forms are assumed to be the same as in the related *trans*-compounds, except for the relations between the terminal groups.[9]

Table 1. The molecular configurations used[a)]

Substituent X	Bond distance (Å)		Bond angle (degree)
	C–C	C–X	∠CCX
-CH_3	1.34	1.54	120
-Cl	1.34	1.72	123
-Br	1.34	1.85	121
-I	1.34	2.05	122

a) CH=1.07Å, ∠CCH=120° for all the compounds.

Results and Discussions

Charge and Energy. The calculated π net charges and π bond orders are presented in Table 2, together with the net charges and E_{AB} values[4,11–13] for all valence electrons. The table indicates that the π delocalization is slightly stronger in *cis*-form than in its *trans* isomer, but the σ charges concentrate a little more on the halogen atoms of the *cis*-form than in the *trans*-forms. It is recognized that the E_{AB} values reflect the substituent effect, that is, the CC and CH bonds in substituted ethylenes are weakened compared with those in ethylene, but different tendencies between the results in Table 2 and the ones predicted by electronegativity for halogen atoms are indicated. These points will be discussed by more refined calculations.

Table 2. The charges and bond orders of 1,2-dihalogenated ethylenes

(a) π Net charge and π bond order

Compounds		π net charge		π bond order	
		C	X	C–X	C–C
Cl[a)]	*t*	−0.039	+0.039	0.193	0.961
	c	−0.042	+0.042	0.199	0.958
Br[a)]	*t*	−0.045	+0.045	0.208	0.955
	c	−0.049	+0.049	0.216	0.951
I[a)]	*t*	−0.044	+0.044	0.204	0.956
	c	−0.046	+0.046	0.208	0.954

(b) Net charge and E_{AB} value (eV) for the valence shell

Compound		Net charge			E_{AB} (eV)		
		C	X	H	C–C	C–X	C–H
Ethylene		−0.016		+0.008	36.46		22.94
Cl	*t*	+0.197	−0.217	+0.020	32.45	18.01	20.98
	c	+0.197	−0.221	+0.025	32.51	17.98	21.01
Br	*t*	+0.055	−0.121	+0.066	33.13	16.48	21.49
	c	+0.065	−0.130	+0.065	33.23	16.39	21.37
I	*t*	+0.037	−0.055	+0.018	32.89	15.16	21.28
	c	+0.046	−0.059	+0.013	32.80	15.23	21.27

a) The notations, Cl, Br, and I to the dichloro-, dibromo- and diiodoethylenes, *t* and *c* are *trans*- and *cis*-compounds, respectively.

Table 3. The U_P values for atoms in chloroethylenes

Compound	AO electron density			U_P values[a)]	
	π	$\bar{\pi}$	σ	Calcd	Obsd
1-Cl	1.958	1.973	1.439	0.527	0.611
1,1-DiCl	1.956	1.956	1.447	0.508	0.717
1,2-DiCl-*t*	1.961	1.974	1.404	0.563	0.649
1,2-DiCl-*c*	1.958	1.974	1.411	0.550	0.638

a) $U_P=\left(\frac{\pi+\bar{\pi}}{2}\right)-\sigma$

b) See Ref. 14.

Different shifts in the *cis*- and *trans*-dichloroethylenes are observed by the PQR measurement;[14] that is, the nuclear quadrupole coupling constants of the Cl^{35} in the *cis*-form are smaller than these in the *trans*-isomer. The values of the PQR U_p values (the number of unbalances electrons) of Cl atoms in various chlorinated ethylenes are estimated by the approximation derived by Townes and Dailey.[15] The results obtained are listed in Table 3, together with the π, $\bar{\pi}$, and σ AO charges. (The $\bar{\pi}$ AO is perpendicular to the C–Cl bond and is on the molecular plane.) The calculated difference in U_p values in the *cis*- and *trans*-forms is in good agreement with the observed value,

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[7] As for 2-butene, the results with $K=0.9$ are in better accordance with the observed values.

[8] "Tables of Interatomic Distances and Configurations in Molecules and Ions," ed. by L. E. Sutton, The Chem. Soc., London (1956, 1965).

[9] As to the *cis*-dichloroethylene, it is suggested in Refs, 10 and 15 that this form may be staggered, that is, the two C–Cl bonds deviate out of the molecular plane. But this staggered form is calculated to be more unstable than its planar form, 0.02 eV at 5° and 0.13 eV at 15°. Thus, we do not consider this form, hereafter.

[10] S. Saito, This Bulletin, **35**, 1483 (1962).

[11] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

[12] H. Konishi, H. Kato, and T. Yonezawa, This Bulletin, **43**, 1676 (1970).

[13] E_{AB} is defined as follows: $E_{AB}=\sum_{r}^{\text{on A}}\sum_{s}^{\text{on B}}P_{rs}(H_{rs}^{c}+F_{rs})$, where the AO's r and s are belonging to the atom A and B, respectively.
P_{rs} is the bond order of r–s pair, and H_{rs}^{c} and F_{rs} are the off-diagonal r–s elements of core resonance integral and Fock operator, respectively. See Refs. 4 and 11.

[14] *E.g.*, "Constants of Organic Compounds," ed. by M. Kotake, Asakura (1963), p. 491.

[15] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

Table 4. Orbital energies of some chloroethylenes (eV)

Vinyl Chloride				1,1-Dichloroethylene			
Calcd		Obsd[a]		Calcd		Obsd[a]	
$11\pi^*$	$+0.56$	—	—	$14b_2\sigma^*$	$+0.22$	—	—
$10\sigma^*$	$+0.49$	—	—	$13b_1\pi^*$	$+0.18$	—	—
9π	-11.86	$a''\pi$	-10.18	$12b_1\pi$	-11.98	π	-10.00
$8n$	-13.31	$a'n$	-11.72	$11a_1n$	-13.74	n	-11.67
7π	-14.68	$na''\pi$	-11.87	$10b_2n$	-14.12	n	-12.17
6σ	-14.88	$a'\sigma$	-13.14	$9a_2\pi$	-14.21	$b_1\pi$	-12.51
				$8b_2\sigma$	-15.47	σ	-13.7
				$7b_1\pi$	-15.90	σ	-14.24

trans-Dichloroethylene				*cis*-Dichloroethylene			
Calcd		Obsd[a]		Calcd		Obsd[a]	
$14b_g\pi^*$	$+1.03$	—	—	$14a_2\pi^*$	$+0.06$	—	—
$13b_u\sigma^*$	-1.01	—	—	$13a_1\sigma^*$	-0.56	—	—
$12a_u\pi$	-11.63	π	-9.81	$12b_1\pi$	-11.57	π	-9.83
$11a_gn$	-13.34	b_un	-11.86	$11a_1n$	-13.18	b_2n	-11.71
$10b_un$	-14.14	$b_g\pi$	-11.93	$10b_2n$	-13.87	$a_2\pi$	-11.85
$9b_g\pi$	-14.97	a_gn	-12.06	$9a_2\pi$	-14.14	a_1n	-12.09
$8a_g\sigma$	-14.97	$a_u\pi$	-12.61	$8b_2\sigma$	-15.06	π	-12.51
$7a_u\pi$	-15.45	σ	-13.85	$7b_1n$	-15.33	σ	-13.72

a) Ref. 16.

but the errors in absolute values between the calculated and observed are over 20% in magnitude. As to these discrepancies, the table suggests that they are mainly due to the large AO charges on the Pσ AO's on the chlorine atoms. Further, the disorder in 1,1-dichloroethylene may be partially caused by the neglect of the Cl–Cl interaction.

Recently, the photoionization spectra of several chlorinated ethylenes were presented, and the symmetry assignments of some MO's were made; the highest occupied MO's in these compounds are of the π type, while the second lower group MO's are lone-pair MO's localized on the chlorine atoms.[16] In Table 4, the observed and calculated MO energies are summarized. The calculated energy values are about 2 eV lower than the observed values, but the orbitals sequences almost coincide. The symmetry assignments partially disagree with each other, especially for the lone-pair-type MO's. In order to reexamine this point, the calculated partial atom charges of the related MO's are collected in Table 5, together with the chlorine AO densities. Our results show that the 10 and 11 MO's are both of the lone-pair type in dichloroethylenes. The latter MO has the a_g symmetry in *trans* and the a_1 symmetry in *cis*-dichloroethylene, and C–Cl anti-bonding and Cl–Cl bonding; on the other hand, the formes MO is b_u in *trans*- and b_2 in *cis*-, and is C–Cl bonding and Cl–Cl anti-bonding. For 1,1-dichloroethylene, the same tendency is obtained as may be seen in the table, in spite of the stronger Cl–Cl interaction. Accordingly, it may be said that the stabilization of these two types

Table 5. The partial atomic charge densities in lone-pair-type MO's in dichloroethylenes

		Partial atomic charges			$\bar{\pi}$AO charge
		H	C	Cl	Cl(π)
trans-	$11a_gn$	0.10	0.12	0.78	(0.77)
	$10b_un$	0.02	0.01	0.97	(0.95)
	$8a_g\sigma$	0.16	0.17	0.76	(0.01)
cis-	$11a_1n$	0.07	0.10	0.83	(0.81)
	$10b_2n$	0.03	0.02	0.95	(0.90)
	$8a_1\sigma$	0.09	0.16	0.75	(0.01)
1,1-	$11a_1n$	0.02	0.14	0.84	(0.64)
	$10b_2n$	0	0.01	0.99	(0.84)
	$8b_2\sigma$	0.10	0.15	0.75	(0.03)

Table 6. The energy diferences between the *cis*- and *trans*-isomers

Substituent	ΔE (kcal/mol)[a]	
	Calcd	Obsd
-CH_3	-0.1	-1.0
-Cl	$+2.3$	$+0.5$[b]
-Br	$+3.9$	—
-I	$+0.2$	-0.6

a) $\Delta E = E(trans) - E(ci)$
b) Ref. 10, 18.
c) Ref. 19.

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16) R. F. Lake, and H. Thompson, *Proc. Roy. Soc. London*, **A 315**, 323 (1970).

TABLE 7. SOME LOWER ELECTRONIC TRANSITION ENERGIES (eV) AND MOMENTS (Å, IN PARENTHESES) OF CHLORINATED ETHYLENES

		CH_2CHCl	CH_2CCl_2	*t*-CHClCHCl	*c*-CHClCHCl	$CHClCCl_2$	CCl_2CCl_2
π-σ	S[a]	5.23(0.138)	5.15(0.0)	4.04(0.0)	4.35(0.180)	4.38(0.071)	3.82(0.0)
	T	4.85	4.91	3.63	4.00	4.04	3.56
π-π^*	S	6.68(0.961)	6.44(0.980)	6.21(1.038)	6.13(1.001)	6.31(1.075)	6.46(1.074)
	T	4.17	3.95	3.81	3.82	3.99	4.38
π-π^*	S	7.63(0.017)	7.64(0.010)	7.19(0.0)	7.10(0.0)	7.64(0.015)	8.05(0.0)
	T	7.54	7.53	7.09	7.01	7.55	7.97
n-σ^*	S	7.06(0.271)	7.43(0.018)	6.38(0.356)	6.70(0.399)	7.28(0.564)	7.17(0.837)
	T	6.61	7.04	6.00	6.30	6.78	6.48
π-π^*	S	9.24(0.355)	8.13(0.658)	8.88(0.0)	8.66(0.0)	8.96(0.479)	9.23(0.575)
	T	8.26	7.46	8.50	8.23	8.63	8.04

a) The notations S and T refer to the singlet and triplet transition.

of lone-pair MO's depends mainly on the C–Cl bonding character and not on the Cl–Cl character, as was pointed out in our previous paper.[3] It is hoped that this discrepancy will be reinvestigated both theoretically and experimentally. Further, it is noticed that the lower vacant MO's are of the σ^* type and the strongly C–Cl antibonding. This result may be correlated to the ease of the C–Cl bond clevage by the polarographic reduction, as was shown by our previous results obtained by simple LCAO MO treatment.[17]

The energy differesces between the *cis*- and *trans*-isomers are listed in Table 6, together with the observed values,[10,18] where E is $E=E(trans)-E(cis)$; that is, the negative value of E indicated that the *trans*-isomer is more stable than the *cis*-form. The results calculated for 2-butene and dichloroethylenes accord with the observed values, but in the diiodo-compounds the results contradict each other.[19]

Electronic Transition Energy. In Table 7, the calculated lower electronic transition energies and moments for the chlorinated ethylenes are summarized. As to the lowest π–π^* singlet transition energies, the agreements between the calculated and observed values[18,20] are excellent: CH_2CHCl: 6.68 (6.70), CH_2CCl_2: 6.44 (6.45), *t*-CHClCHCl: 6.21 (6.36), *c*-CHClCHCl: 6.13 (6.53), $CHClCCl_2$: 6.31 (6.32), CCl_2CCl_2: 6.46 (6.29), where the numbers in parenthes are the observed values.[18,20] The other types of transitions have not yet been assigned by means of observations, but it is interesting that the lowest transitions obtained are π-σ^* transitions, as was suggested in our previous paper.[17]

The lowest π–π^* transition energies and oscillator strength values (Å) for various *cis*- and *trans*-isomers are collected in Table 8. The calculated values for the π–π^* transition energy in *cis*-isomers are considerably smaller than the observed values, and the order of magnitude for *cis*- and *trans*-isomers does not agree with the observations. As to the transition moments, the calculations show that values in the *trans*-isomers are larger than in *cis*-isomers. This tendency is to be expected from the symmetry consideration for these isomers; that is, the lowest π–π^* transitions belong to the b_u irreducible representation in the *trans*-isomer (C_{2h}) and to the b_2 in the *cis*-isomer (C_{2v}). Thus the components of the transition moment are x and y in b_u, and y in b_2 (the direction of y is parallel to the central CC bond and x is perpendicular to this bond), and the moment values (y) are nearly equal for the two isomers. Therefore, the differences between the *cis*- and *trans*-isomers are dependent on the x component values.

TABLE 8. THE LOWEST π-π^* TRANSITION ENERGIES OF SOME *cis*- AND *trans*-ISOMERS

Compound[a]	Calcd			Obsd
	Transition energy		Transition moments (Å)	Transition energy
	Singlet	Triplet		Singlet(Tripler)
t-CH_3	6.33 (6.90)[d]	3.80 (4.37)	0.984 (0.988)	6.97(4.07)[b]
c-CH_3	6.30 (6.87)	3.78 (4.35)	0.948 (0.961)	7.10[b]
t-Cl	6.21	3.81	1.038	6.36[c]
c-Cl	6.13	3.82	1.001	6.53[c]
t-Br	5.66	4.19	1.002	—
c-Br	5.49	4.11	0.923	—
t-I	5.38	4.34	0.984	—
c-I	5.27	4.26	0.876	—

a) The notations *t*- and *c*-, indicate *trans*- and *cis*-substituted ethylene, respectively.

b) M. Itoh, R. S. Mulliken, *J. Phys. Chem.*, **73**, 4332 (1969); A. J. Merer, R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

c) Refs. 18, 20.

d) In 2-Butene, the values in parentheses are obtained by $K=0.9$.

The Rotational Barrier. It is well known that the *cis*-*trans*-isomerization of ethylenic compounds occurs through the perpendicular configuration, in which the

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[17] K. Fukui, K. Morokuma, H. Kato, and T. Yonezawa, This Bulletin, **36**, 217 (1963).

[18] J. P. Teegan and A. D. Walsh, *Discuss. Faraday Soc.*, **47**, 1 (1951).

[19] H. Steinmetz and R. M. Noyes, *J. Amer. Chem. Soc.*, 4141 (1952).

[20] A. D. Walsh, *Discuss. Faraday Soc.*, **41**, 35 (1945); A. D. Walsh and P. A. Warsop, *Trans. Faraday Soc.*, **64**, 1418 (1968); A. D. Walsh, P. A. Warsop, and J. A. B. Whiteside. *ibid.*, **64**, 1432 (1968).

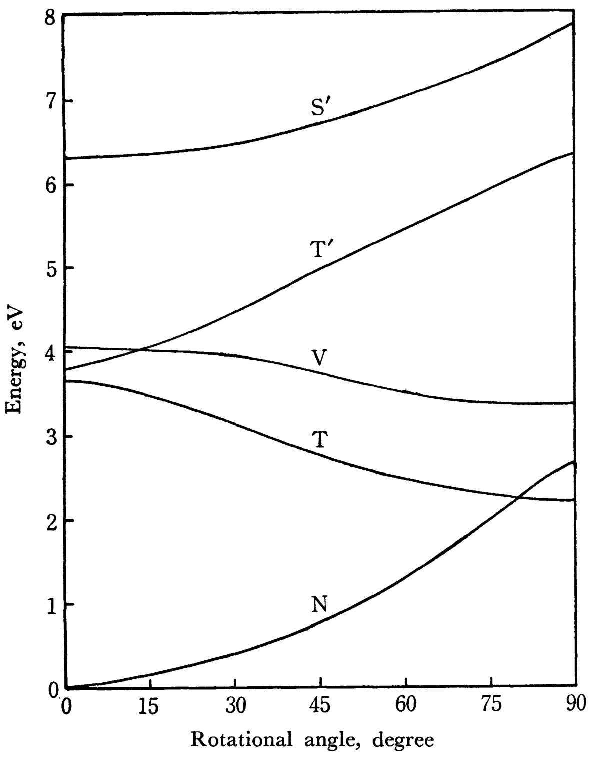

Fig. 1. Rotational energy barrier of *trans*-1,2-dichloroethylene.

triplet state is most stable.[1,21,22] In this section, we will present the potential energy changes caused by the rotation around the central CC double bond, where the rotational configurations are assumed to be unchanged, as in the planar *trans*-form, except for the rotational angles.[23] In Fig. 1, the energy changes for various rotational angles in the *trans*-dichloroethylene are plotted, the N, T, and V notations are the ground state and the lowest triplet and singlet states respectively. It may be noticed that the T and V states, in the twisted configurations are constructed mainly by the lowest π–π^* and π–σ^* excited states in the planar form.

TABLE 9. THE FORCE CONSTANTS FOR TWISTING VIBRATIONS IN *cis*- AND *trans*-SUBSTITUTED ETHYLENE (mdyn Å/rad)

	Calcd	Obsd[a]
Ethylene	0.128	0.136
t-CH_3	0.158	0.162
c-CH_3	0.130	—
t-Cl	0.095	0.168
c-Cl	0.092	0.161
t-Br	0.098	—
c-Br	0.099	—
t-I	0.090	—
c-I	0.089	—

a) K. S. Pitzer and J. L. Hollenberg, *J. Amer. Chem. Soc.*, **76**, 1493 (1954).

By utilizing the obtained potential curves, the estimations of the force constant for the twisting vibration around a CC bond are made. The results obtained are presented in Table 9. Considering the approximations used, the agreements between them are fairly good, but the values in halogenated compounds are somewhat smaller.

At the twist angle of 90°, the above-mentioned states are labelled by the suffix m, N_m, T_m, and V_m; these energy values are listed in Table 10, together with the the angle, θ_1, at which the N and T states cross. In Fig. 2, the outlines of these state energy curves are given. From the table it is clear that the singlet and triplet energies decrease to minima at the perpendicular configuration, and that, in this state, the T_m states are the lowest. Further, the calculations show that the shapes of the potential energy curves of *cis*- and *trans*-isomers are not very different, and that the crossing of T and N states occurs near 90°. Thus, it may be said that the intermediate triplet states through the *cis*-*trans*-isomerization are common to both isomers. This result accords with the experimental conclusions for the *cis*-*trans*-isomerization in dichloroethylene.[22] It may, however, be noticed that since the R_m and V_m states converge to the degenerate state in ethylene, more knowledge of the configuration interaction will be necessary before we can discuss these states more quantitatively.

TABLE 10. THE POTENTIAL ENERGIES (eV) IN PERPENDICULAR CONFIGURATIONS[a]

		T_m	N_m	V_m	θ_1
	t-CH_3	2.60	3.24	4.03	82°
	t-Cl	2.41	2.96	3.64	79°
	t-Br	2.33	2.51	3.25	82°
	t-I	2.47	2.68	3.32	85°
Ethylene	Calcd[b]	3.24	3.60	9.72	79°
	Obsd[c]	2.8	4.13	5.68	—

a) The reference energy of these states is chosen as that of the planar *trans*-form.
b) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).
c) R. McDiarmid and E. Charney, *ibid.*, **47**, 1517 (1967).

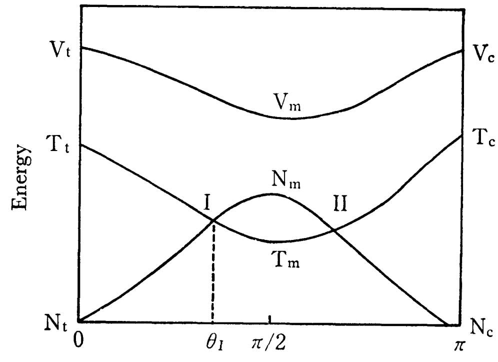

Fig. 2. A sketch of potential energy diagram.

The calculations have been carried out on the FACOM 230—60 Computer of Kyoto University.

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[21] A. J. Merer and R. S. Mulliken, *Chen. Revs.*, **69**, 639 (1969).

[22] Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964).

[23] In the perpendicular configurations of these compounds, the molecular coordinates may change from the planar ones, but no accurate observed values have yet been presented.