

## EFFECT OF THE ELECTRIC FIELD ON MOLECULAR STRUCTURE IN THE MNDO APPROXIMATION

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Received October 17th, 1985

The MNDO method has been modified to include the effect of external electric field. It has been applied to calculate the electronic structure of methane, carbon monoxide, acetylene, ammonia, ethylene, acetaldehyde, and methylamine in the electric field of various intensities. The results show that the properties of molecules are considerably influenced by the electric field. This is manifested in the distribution of electrons on the one hand, and in the change of orientation of a molecule with respect to the direction of the electric field on the other hand. The results are in a qualitative agreement with previous results of CNDO, INDO, and *ab initio* methods.

In many physical and biochemical systems, external electric field is of great importance. For example in electrochemistry, intense electric fields are reached on the metal/electrolyte interface. Their magnitudes vary within  $10^7$ – $10^9$   $\text{Vm}^{-1}$ . The potential differences between surfaces of biological membranes give rise to electric fields of intensities up to  $10^7$   $\text{Vm}^{-1}$ . Such strong electric fields can influence structures of molecules in biomembranes and consequently their biological functions. Strong electric fields also exert influence on physical sorption, chemisorption, catalysis, and enzymatic processes, where they reach intensities up to  $10^{10}$   $\text{Vm}^{-1}$  and can considerably affect the course of such processes. Electric fields can also be produced by any ionic or molecular systems. Strong electrostatic fields up to  $10^9$   $\text{Vm}^{-1}$  are used in mass spectroscopy, where they strongly influence decompositions of molecules.

The theory of molecular systems subject to the influence of external electric field is not a very developed field of quantum chemistry. Nevertheless, using semiempirical methods to calculate changes of various physical properties of simple molecules and ions affected by strong electric fields, several interesting results have been obtained.

Lorquet and Hall<sup>1,2</sup> explained dissociation processes of aliphatic hydrocarbons in uniform electric fields of various intensities. The influence of electric field on methanol was studied by Bounds, Hincliffe, and Barber<sup>3</sup> using the INDO method. The effect of electric fields on HF,  $\text{CH}_3\text{Cl}$ ,  $\text{H}_2\text{O}$ , and some ions was observed by Drussbach and Schmittinger<sup>4-6</sup> using the *ab initio* method. Aleksankin and coworkers studied the fragmentation of positive molecular ions<sup>7-9</sup> and behaviour of acetaldehyde<sup>10</sup>, dioxane<sup>11</sup>, and methylamine<sup>12</sup> in external electric fields by the CNDO/2 method. Pancfř and Zahradník<sup>13</sup> applied the modified INDO method to ethylene. The *ab initio* method was applied by Nakatsuji<sup>14</sup> to methane, ethylene, ammonia, and carbon monoxide in the investigation of structure and geometry in the external electric field.

In this paper, the operator of interaction with the external electric field has been included into the MNDO method<sup>15</sup> and has been applied to CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, acetaldehyde, and methylamine. The field intensity has been varied in the range from 0 to 10<sup>10</sup> V m<sup>-1</sup>.

### THEORETICAL

In the presence of external electrostatic field the Hartree-Fock matrix elements can be written as

$$F_{\mu\nu} = F_{\mu\nu}^0 - e \cdot \mathbf{F} \cdot \langle \mu | \mathbf{r} | \nu \rangle, \quad (1)$$

where  $F_{\mu\nu}^0$  is the corresponding term for zero external field,  $e$  is the charge of electron,  $\mathbf{F}$  is the intensity of the electric field, and  $\langle \mu | \mathbf{r} | \nu \rangle$  are the matrix elements of projections of the radius-vector onto the direction of the electric field vector. Expanding the relation (1), the Hartree-Fock matrix elements become

$$F_{\mu\nu} = H_{\mu\nu} - e \cdot \mathbf{F} \cdot \langle \mu | \mathbf{r} | \nu \rangle + \sum_A \sum_{\lambda, \sigma \in A} [P_{\lambda\sigma}(\mu\nu | \lambda\sigma) - 0.5(\mu\lambda | \nu\sigma)]. \quad (2)$$

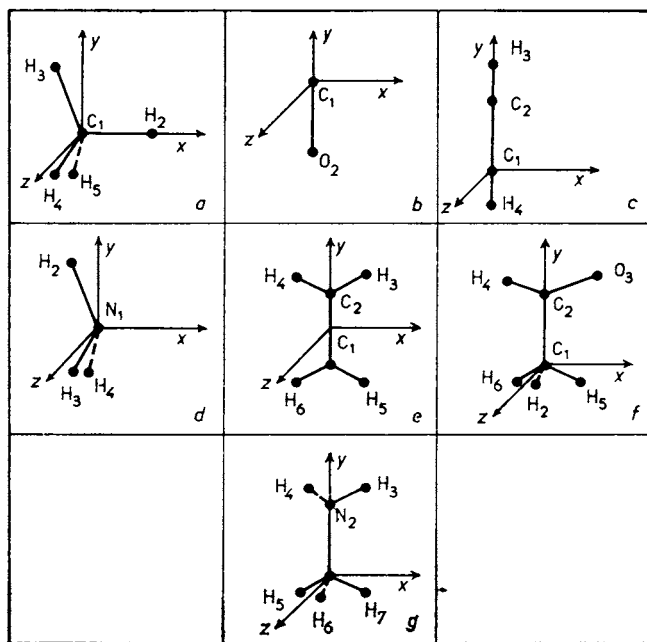


FIG. 1

Orientation of molecules with respect to the coordinate system

The expression for the total energy of a molecule taking into account the influence of external electric field acquires the form

$$E = 0.5 \sum_{\mu} \sum_{\nu} P_{\mu\nu} [H_{\mu\nu} + F_{\mu\nu} - e \cdot \mathbf{F} \cdot \langle \mu | \mathbf{r} | \nu \rangle] + \sum_{A < B} E_{AB}^{\text{core}} - \mathbf{F} \sum_A Z_A \mathbf{R}_A \quad (3)$$

For the sake of clarity of the following text, Fig. 1 is used to show the orientation of molecules with respect to the coordinate system.

## RESULTS AND DISCUSSION

Two orientations of the electric field have been studied in the case of methane, namely, along the C—H bond and along the axis of the H—C—H bond angle, both with the field in the positive and negative directions of axes (Fig. 1a). The field intensities of 0.103, 1.03, and 10.33 · 10<sup>10</sup> V m<sup>-1</sup> have been applied. There is not a big difference between the energies of given orientations at equal intensities.

TABLE I

Calculated characteristics of the methane molecule in electric fields of various intensities

Field intensity 10 <sup>10</sup> V m <sup>-1</sup>	Total energy kJ mol <sup>-1</sup>	Ionization potential eV	Dipole moment 10 <sup>-30</sup> C m	Total charges of atoms in units of the proton charge				
				C <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>
0.0	-17 858.87	13.87	0.0	0.070	-0.017	-0.017	-0.017	-0.017
Field along the <i>x</i> axis								
10.3	-18 776.10	10.56	22.77	0.066	0.591	-0.219	-0.219	-0.219
1.03	-17 864.03	13.38	0.81	0.059	-0.002	-0.019	-0.019	-0.019
0.103	-17 858.12	13.71	0.17	0.069	-0.021	-0.016	-0.016	-0.016
-10.3	-18 677.96	12.89	22.32	0.140	-0.748	0.203	0.203	0.203
-1.03	-17 863.25	13.79	1.06	0.081	-0.049	-0.010	-0.010	-0.010
-0.103	-17 858.03	13.78	0.18	0.071	-0.026	-0.015	-0.015	-0.015
Field along the axis of the H <sub>3</sub> C <sub>1</sub> H <sub>2</sub> angle								
10.3	-18 415.85	10.64	15.83	0.369	0.152	0.220	-0.372	-0.372
1.03	-17 863.69	13.49	0.87	0.064	-0.010	-0.002	-0.026	-0.026
0.103	-17 858.10	13.72	0.08	0.070	-0.022	-0.014	-0.017	-0.017
-10.3	-18 435.16	10.94	17.75	0.475	-0.452	-0.421	0.199	0.199
-1.02	-17 863.21	13.67	0.91	0.076	-0.037	-0.029	-0.005	-0.005
-0.103	-17 858.05	13.76	0.16	0.071	-0.025	-0.017	-0.014	-0.014

A stronger influence is observed for the positive direction of the electric field vector. In the direction of the C—H bond, the influence of the field grows as its intensity increases. The results obtained for  $F = \pm 10 \cdot 3 \cdot 10^{10} \text{ V m}^{-1}$  significantly differ from those calculated for the other intensities. For this intensity, reverse polarization of the C—H bond occurs. While at lower intensities the positive charge is localized on the carbon atom and the negative charge on the hydrogen atoms, in this case the charge distribution is reversed. Thus a large dipole moment is induced. The corresponding results are given in Table I.

The most interesting results for carbon monoxide are obtained with the electric field parallel to the C—O bond (Table II, Fig. 1*b*). Comparing the positive and negative directions of the field, it can be seen that the most stable orientation corresponds to the negative direction. For all intensities and orientations of the field, the positive charge is localized on the carbon atom and the negative charge on the oxygen atom, except the case of  $F_y = -10 \cdot 3 \cdot 10^{10} \text{ V m}^{-1}$  when the polarization is reversed.

In the case of acetylene, the orientation of the electric field along the C—C bond is of interest. Simultaneously, this is the most stable orientation of the molecule

TABLE II  
Calculated characteristics of the carbon monoxide molecule in electric fields of various intensities

Field intensity $10^{10} \text{ V m}^{-1}$	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge	
				C <sub>1</sub>	O <sub>2</sub>
0·0	-43 286·82	13·43	0·65	0·213	-0·213
Field along the <i>x</i> axis					
10·3	-44 610·96	10·31	13·16	0·313	-0·313
1·03	-43 305·27	13·40	2·13	0·215	-0·215
0·103	-43 287·01	13·43	0·68	0·213	-0·213
-1·03	-43 305·27	13·40	2·13	0·215	-0·215
Field along the <i>y</i> axis					
10·3	-44 385·22	8·95	30·82	1·248	-1·248
1·03	-43 261·09	12·90	3·18	0·317	-0·317
0·103	-43 283·22	13·38	0·90	0·224	-0·224
0·00103	-43 286·45	13·42	0·67	0·214	-0·214
-10·3	-44 714·34	6·25	25·33	-0·971	0·971
-1·03	-43 335·13	13·80	1·86	0·107	-0·107
-0·103	-43 290·66	13·47	0·40	0·203	-0·203

in external electric field. The polarization of the C—C bond increases as the field intensity grows. For the intensities  $F_y = 0.103$  and  $0.0103 \cdot 10^{10} \text{ V m}^{-1}$  and  $F_x = 0.0103$  and  $0.103 \cdot 10^{10} \text{ V m}^{-1}$ , the negative charge is localized on both carbon atoms and the positive charge on all the other atoms. For the intensity  $F_y = 10.3 \cdot 10^{10} \text{ V m}^{-1}$  the  $C_1$  atom is negative (Fig. 1c) and all the other atoms are positive, for  $F_y = -10.3 \cdot 10^{10} \text{ V m}^{-1}$  the values for  $C_1$  and  $H_3$  are reversed in consequence of symmetry, for  $F_y = 10.3 \cdot 10^{10} \text{ V m}^{-1}$  the  $C_1$  and  $H_4$  atoms are negative and  $C_2$  and  $H_3$  are positive. This is caused by the strong influence of the electric field on the  $\text{C}\equiv\text{C}$  bond. For  $F_x = 10.3 \cdot 10^{10} \text{ V m}^{-1}$  negative charge is localized on both hydrogen atoms while the carbon atoms are positive (Table III).

Table IV shows that the most stable orientation of the ammonia molecule corresponds to the field intensity in the negative direction of the  $x$  axis (see Fig. 1d) for which the energies are lower than for the opposite orientation of the field. However, this is inconsistent with the results of Nakatsuji<sup>14</sup> who drew just the contradictory conclusion. This contradiction will require further detailed investigation.

As a consequence of symmetry of the ethylene molecule (Fig. 1e, Table V), it is

TABLE III

Calculated characteristics of the acetylene molecule in electric fields of various intensities

Field intensity $10^{10} \text{ V m}^{-1}$	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge			
				$C_1$	$C_2$	$H_3$	$H_4$
0.0	-27 177.14	11.02	0.0	-0.155	-0.155	0.155	0.155
Field along the $x$ axis							
10.3	-28 683.57	10.02	20.62	0.050	0.050	0.050	0.050
1.03	-27 189.25	10.99	1.31	-0.155	-0.155	0.155	0.155
-1.03	-27 189.25	10.99	1.31	-0.155	-0.155	0.155	0.155
0.103	-27 177.26	11.03	0.13	-0.155	-0.155	0.155	0.155
0.0103	-27 177.14	11.03	0.01	-0.155	-0.155	0.155	0.155
Field along the $y$ axis							
10.3	-29 585.92	4.86	79.91	-0.516	0.550	0.937	-0.980
1.03	-27 193.80	10.43	3.38	-0.315	0.007	0.141	0.168
-1.03	-27 193.80	10.43	3.38	0.007	-0.315	0.168	0.141
0.103	-27 177.31	10.97	0.34	-0.171	-0.138	0.153	0.156
0.0103	-27 177.14	11.02	0.03	-0.156	-0.153	0.154	0.155

sufficient to study for a chosen orientation of the molecule in the coordinate system only the cases with the electric field in the positive directions of axes. Among all orientations of the ethylene molecule, the most stable one is for the field along the  $y$  axis (*i.e.* the direction of the C—C bond, see Fig. 1e) and the least stable one for the field vector parallel to the  $x$  axis (Table V).

Increasing the intensity  $F_x$  and  $F_z$ , the energy decreases and the induced dipole moment grows; the charge of the carbon atoms is negative and its value decreases as the field intensity grows. The C—C bond becomes more polarized and the total energy decreases as the field intensity is increased. At the field intensity of  $2.06 \cdot 10^{10} \text{ V m}^{-1}$  the electron density on the  $C_2$  atom is reduced so much that the atom becomes positive.

The acetaldehyde molecule has been studied in two conformations referred as *AA1* and *AA2*. Fig 1f shows the *AA1* conformation whose dihedral angle  $H_5C_1C_2O_3$  equals  $30^\circ$ , while the angle of the *AA2* conformation is zero. The  $C_1C_2O_3$  angle lies in both cases in the  $xy$  plane. Calculations have been performed for intensities of the electric field of  $0.103$  and  $1.103 \cdot 10^{10} \text{ V m}^{-1}$  along the  $y$  axis. Both conformations have been rotated about the  $x$  axis (curve 1 in Figs 2 and 3) and about the  $z$  axis (curve 2 in Figs 2 and 3). As the course of these curves is similar for both conformations, we shall further discuss only the conformation with dihedral angle of  $30^\circ$  and mention the other one only when necessary. Changes of the total energy of the molecule and of its dipole moment depending on the orientation in the electric

TABLE IV  
Calculated characteristics of the ammonia molecule in electric fields of various intensities

Field intensity $10^{10} \text{ V m}^{-1}$	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge			
				$N_1$	$H_2$	$H_3$	$H_4$
0.0	-24 145.91	11.19	5.85	-0.228	0.076	0.076	0.076
Field along the $x$ axis							
10.3	-24 212.28	10.05	13.73	0.816	-0.272	-0.272	-0.272
1.03	-24 057.15	10.62	5.55	-0.205	0.068	0.068	0.068
0.103	-24 136.86	11.13	5.82	-0.226	0.075	0.075	0.075
0.0103	-24 145.00	11.18	5.85	-0.228	0.076	0.076	0.076
-10.3	-25 235.95	13.55	8.85	-0.473	0.158	0.158	0.158
-1.03	-24 238.44	11.71	6.16	-0.253	0.084	0.084	0.084
-0.103	-24 154.99	11.24	5.88	-0.231	0.077	0.077	0.077
-0.0103	-24 146.81	11.19	5.86	-0.229	0.076	0.076	0.076

TABLE V  
Calculated characteristics of the ethylene molecule in electric fields of various intensities

Field intensity $10^{10} \text{ V m}^{-1}$	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge					
				C <sub>1</sub>	C <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>
0.0	-30 086.37	10.18	0.00	-0.080	-0.080	0.040	0.040	0.040	0.040
Field along the z axis									
10.3	-31 641.06	10.03	19.70	0.177	0.177	-0.088	-0.088	-0.088	-0.088
1.03	-30 101.70	10.17	1.65	-0.070	-0.079	0.040	0.040	0.040	0.040
0.103	-30 086.53	10.18	0.16	-0.080	-0.080	0.040	0.040	0.040	0.040
0.0103	-30 086.38	10.18	0.02	-0.080	-0.080	0.040	0.040	0.040	0.040
Field along the x axis									
10.3	-31 216.52	10.17	43.61	0.170	0.170	0.439	-0.609	0.439	-0.609
1.03	-30 093.72	10.18	1.06	-0.079	-0.079	0.046	0.032	0.046	0.032
0.103	-30 086.45	10.18	0.11	-0.080	-0.080	0.041	0.039	0.041	0.039
0.0103	-30 086.38	10.18	0.01	-0.080	-0.080	0.040	0.040	0.040	0.040
Field along the y axis									
10.3	-32 490.18	10.20	81.10	-0.146	0.346	-0.743	-0.743	0.643	0.643
4.12	-30 409.50	10.69	15.03	-0.361	0.205	-0.009	-0.009	0.086	0.086
3.09	-30 270.63	10.46	11.69	-0.313	0.156	0.005	0.005	0.074	0.074
1.03	-30 107.17	10.21	4.08	-0.167	-0.008	0.029	0.028	0.051	0.051
0.515	-30 091.59	10.19	2.05	-0.124	-0.036	0.034	0.034	0.046	0.046
0.0103	-30 086.38	10.18	0.04	-0.081	-0.079	0.040	0.040	0.040	0.040

field characterized by the angle  $\alpha$  ( $\alpha = 0^\circ$  corresponds to the orientation of the molecule shown in Fig. 1f) are given in Figs 2 and 3 and in Tables VI to VIII.

The strongest influence of external electric field can be observed for the rotation about the  $z$  axis due to the permanent dipole moment in the  $xy$  plane. The changes of the total energy (dipole moment) are sine-like (cosine-like). The minimum (maximum) of the total energy (dipole moment) for the rotation about the  $x$  axis is reached when the angle of rotation equals  $180^\circ$  and the maximum of energy (minimum of dipole moment) for  $0^\circ$ . For the rotation about the  $z$  axis, there is an energy minimum and a dipole moment maximum at  $130^\circ$  and an energy maximum and a dipole moment minimum at  $310^\circ$  (this holds for both conformations under investigation). The most stable orientation is with the dipole moment parallel to the external electric field. Rotating the *AA1* conformation about the  $z$  axis at field intensity  $F_y = 0.103 \cdot 10^{10} \text{ V m}^{-1}$  only the oxygen and  $C_1$  atoms are negative while the other atoms are positive. Rotating *AA1* about the  $x$  axis at field intensity  $F_y = 1.03 \cdot 10^{10} \text{ V m}^{-1}$ , the charge changes to positive on the  $C_1$  atom and to negative on the  $H_5$  and  $H_6$  atoms in the area of the energy minimum. For the field intensity of  $1.03 \cdot 10^{10} \text{ V m}^{-1}$ , the charge of  $C_1$  changes to positive and the charge of  $H_5$  to negative when rotating *AA1* about the  $z$  axis in the area of the energy maximum. The polarity of the  $C_1$ ,  $H_5$ , and  $H_6$  atoms of the *AA2* conformation is changed as the molecule rotates

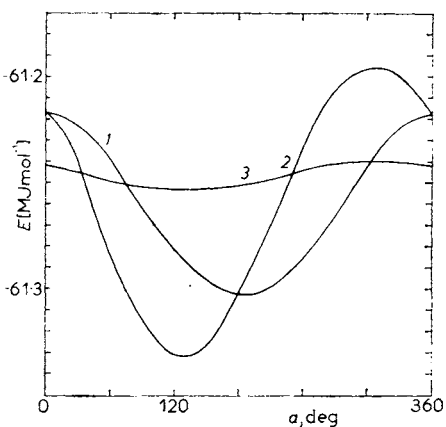


FIG. 2

Changes of the total energy with rotation of acetaldehyde in external electric field. 1 — rotation about the  $x$  axis at  $F_y = 1.03 \cdot 10^{10} \text{ V m}^{-1}$ , 2 — rotation about the  $z$  axis at  $F_y = 1.03 \cdot 10^{10} \text{ V m}^{-1}$ , 3 — rotation about the  $z$  axis at  $F_y = 0.103 \cdot 10^{10} \text{ V m}^{-1}$

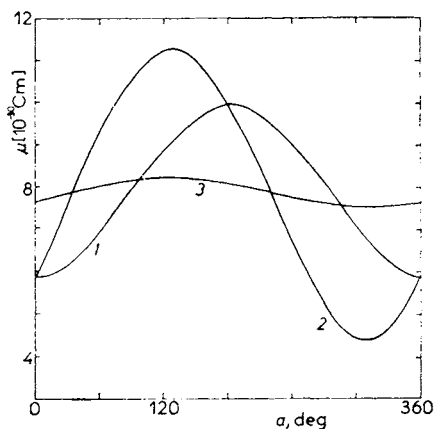


FIG. 3

Changes of the dipole moment with rotation of acetaldehyde in external electric field. Numbering of curves as in Fig. 2



TABLE VI  
Rotation of acetaldehyde about the  $x$  axis. Field intensity  $1.03 \cdot 10^{10} \text{ V m}^{-1}$  along the  $y$  axis

Angle of rotation deg	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge						
				$C_1$	$C_2$	$O_3$	$H_4$	$H_5$	$H_6$	$H_7$
Zero field	-61 246.47	10.87	7.85	-0.026	0.243	-0.286	0.012	0.022	0.012	0.023
0	-61 218.09	9.14	5.85	0.042	0.159	-0.220	0.017	0.004	-0.005	0.003
30	-61 223.97	9.38	6.14	0.033	0.170	-0.229	0.017	0.002	-0.006	0.014
60	-61 240.20	10.03	6.93	0.009	0.200	-0.252	0.015	0.006	-0.003	0.026
90	-61 261.54	10.89	7.94	-0.026	0.241	-0.283	0.012	0.014	0.004	0.038
120	-61 282.16	11.70	8.91	-0.062	0.282	-0.316	0.009	0.025	0.014	0.047
150	-61 297.13	12.27	9.63	-0.089	0.313	-0.340	0.008	0.035	0.023	0.050
180	-61 303.03	12.46	9.94	-0.099	0.324	-0.349	0.008	0.041	0.029	0.045
210	-61 298.39	12.26	9.73	-0.089	0.313	-0.339	0.008	0.043	0.031	0.033
240	-61 284.10	11.70	9.06	-0.062	0.282	-0.314	0.009	0.039	0.027	0.019
270	-61 263.44	10.88	8.08	-0.026	0.240	-0.281	0.012	0.030	0.020	0.005
300	-61 241.61	10.03	7.05	0.008	0.199	-0.250	0.014	0.020	0.011	-0.003
330	-61 224.71	9.37	6.21	0.033	0.170	-0.228	0.016	0.010	0.002	-0.003

TABLE VII  
Rotation of acetaldehyde about the z axis. Field intensity  $1.03 \cdot 10^{10} \text{ V m}^{-1}$  along the y axis

Angle of rotation deg	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge						
				C <sub>1</sub>	C <sub>2</sub>	O <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>
0	-61 218.09	9.14	5.85	0.042	0.159	-0.220	0.017	0.004	-0.005	0.003
30	-61 247.83	9.51	7.56	0.035	0.194	-0.266	0.025	-0.005	0.005	0.008
60	-61 283.08	10.25	9.29	0.011	0.240	-0.315	0.029	0.002	0.016	0.017
90	-61 314.27	11.14	10.60	-0.024	0.286	-0.356	0.029	0.010	0.026	0.028
120	-61 331.01	11.93	11.21	-0.061	0.319	-0.377	0.026	0.022	0.033	0.038
150	-61 326.86	12.40	10.97	-0.089	0.333	-0.375	0.019	0.034	0.034	0.044
180	-61 303.03	12.46	9.94	-0.099	0.324	-0.349	0.008	0.042	0.029	0.045
210	-61 268.11	12.12	8.34	-0.088	0.294	-0.304	-0.006	0.044	0.019	0.040
240	-61 233.42	11.44	6.61	-0.060	0.249	-0.253	-0.014	0.040	0.007	0.031
270	-61 207.88	10.58	5.17	-0.023	0.199	-0.210	-0.014	0.032	-0.004	0.020
300	-61 196.24	9.77	4.42	0.010	0.161	-0.188	-0.006	0.022	-0.011	0.010
330	-61 199.92	9.23	4.66	0.033	0.147	-0.192	0.006	0.012	-0.011	0.004

TABLE VIII  
Rotation of acetaldehyde about the x axis. Field intensity  $0.103 \cdot 10^{10} \text{ V m}^{-1}$  along the y axis

Angle of rotation deg	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge						
				C <sub>1</sub>	C <sub>2</sub>	O <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>
0	-61 242.36	10.71	7.65	-0.019	0.235	-0.280	0.012	0.020	0.010	0.021
30	-61 245.58	10.74	7.82	-0.020	0.236	-0.280	0.012	0.021	0.011	0.021
60	-61 249.09	10.81	7.99	-0.023	0.239	-0.283	0.012	0.022	0.012	0.021
90	-61 251.96	10.90	8.13	-0.026	0.243	-0.286	0.012	0.023	0.013	0.022
120	-61 253.39	10.98	8.19	-0.030	0.247	-0.289	0.011	0.024	0.014	0.023
150	-61 252.99	11.03	8.17	-0.033	0.250	-0.291	0.011	0.024	0.014	0.024
180	-61 250.86	11.05	8.06	-0.033	0.252	-0.292	0.011	0.024	0.014	0.025
210	-61 247.59	11.01	7.89	-0.032	0.250	-0.291	0.011	0.023	0.013	0.026
240	-61 244.08	10.93	7.72	-0.030	0.247	-0.289	0.011	0.022	0.012	0.026
270	-61 241.27	10.85	7.58	-0.026	0.243	-0.286	0.012	0.021	0.011	0.025
300	-61 239.89	10.77	7.51	-0.023	0.239	-0.283	0.012	0.021	0.010	0.024
330	-61 240.29	10.71	7.54	-0.020	0.236	-0.280	0.012	0.020	0.010	0.022

about the  $x$  axis in the area of the energy maximum. Rotating  $AA_2$  about the  $z$  axis at field intensity  $F_y = 1.03 \cdot 10^{10} \text{ V m}^{-1}$ , the polarity of the  $C_1$ ,  $H_4$ ,  $H_5$ , and  $H_7$  atoms is changed. The rotation of acetaldehyde in external electric field was also studied by Aleksankin and coworkers<sup>10</sup> using a modified INDO method. They arrived at a qualitatively similar picture of the influence of the electric field on the orientation of acetaldehyde. However, the results quantitatively differ due to the use of different methods.

In the case of methylamine (Fig. 1g), the  $C_1$  atom has been placed into the origin of the coordinate system and the  $C-N$  bond along the positive direction of the  $y$  axis. Two conformations of this molecule have been studied, the first one with the  $H_3N_2C_1H_6$  dihedral angle equal to  $0^\circ$  and the other one with the dihedral angle of  $60^\circ$ . The electric field vector has been parallel to the  $y$  axis. Results for the conformation with zero dihedral angle are presented. This conformation has been rotated about the  $x$  axis at field intensities  $0.103$  and  $1.03 \cdot 10^{10} \text{ V m}^{-1}$  (Tables IX, X). Changes of the total energy and dipole moment are shown in Figs 4 and 5. There is an energy minimum at  $225^\circ$  for the rotation about the  $x$  axis. This minimum, how-

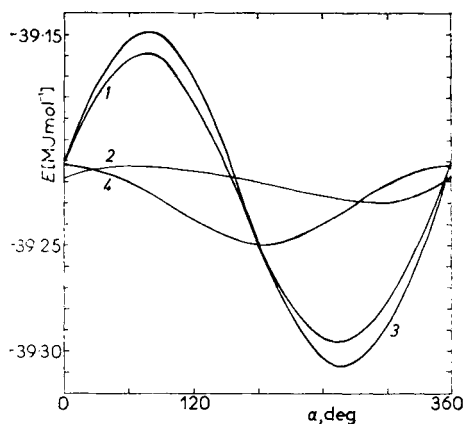


FIG. 4

Changes of the total energy with rotation of methylamine in external electric field. 1 — rotation of the conformation with dihedral angle equal to  $0^\circ$  at  $F_y = 1.03 \cdot 10^{10} \text{ V m}^{-1}$ , 2 — rotation of the same conformation at  $F_y = 0.103 \cdot 10^{10} \text{ V m}^{-1}$ , 3 — rotation of the conformation with dihedral angle equal to  $60^\circ$  at  $F_y = 1.03 \cdot 10^{10} \text{ V m}^{-1}$ , 4 — rotation of the same conformation at  $F_x = 0.103 \cdot 10^{10} \text{ V m}^{-1}$

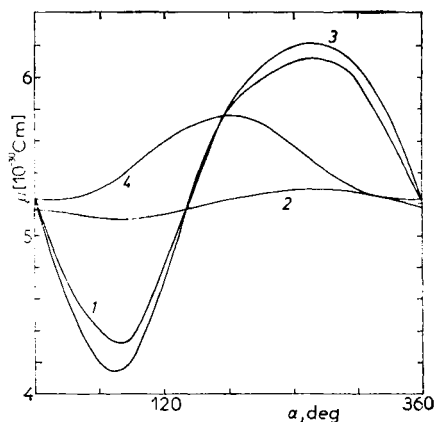


FIG. 5

Changes of the dipole moment with rotation of methylamine in external electric field. Numbering of curves as in Fig. 4

TABLE IX  
Rotation of methylamine about the x axis. Field intensity  $1.03 \cdot 10^{10} \text{ V m}^{-1}$  along the y axis

Angle of rotation deg	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ C m}$	Total charges of atoms in units of the proton charge						
				C <sub>1</sub>	N <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>
Zero field	-39 219.58	10.38	5.19	0.130	-0.307	0.105	0.105	0.007	-0.020	-0.020
0	-39 212.65	9.07	5.22	0.177	-0.331	0.126	0.126	-0.018	-0.040	-0.040
30	-39 180.59	9.04	4.70	0.178	-0.327	0.126	0.115	-0.009	-0.038	-0.047
60	-39 161.07	9.38	4.37	0.165	-0.318	0.122	0.101	0.005	-0.030	-0.045
90	-39 160.69	9.99	4.46	0.139	-0.303	0.112	0.087	0.017	-0.019	-0.034
120	-39 179.99	10.68	4.87	0.110	-0.286	0.100	0.076	0.027	-0.008	-0.020
150	-39 212.78	11.25	5.38	0.088	-0.274	0.088	0.074	0.031	-0.001	-0.007
180	-39 248.99	11.58	5.75	0.078	-0.272	0.081	0.081	0.029	0.002	0.002
210	-39 278.77	11.59	5.98	0.081	-0.280	0.081	0.095	0.021	-0.001	0.004
240	-39 295.05	11.30	6.09	0.097	-0.294	0.087	0.110	0.008	-0.008	0.001
270	-39 294.46	10.75	6.10	0.119	-0.310	0.098	0.122	-0.005	-0.018	-0.006
300	-39 277.45	10.07	5.98	0.144	-0.322	0.110	0.130	-0.016	-0.028	-0.017
330	-39 247.91	9.44	5.68	0.164	-0.329	0.120	0.131	-0.020	-0.037	-0.029

TABLE X  
Rotation of methylamine about the x axis. Field intensity  $0.103 \cdot 10^{10} \text{ V m}^{-1}$  along the y axis

Angle of rotation deg	Total energy $\text{kJ mol}^{-1}$	Ionization potential eV	Dipole moment $10^{-30} \text{ Cm}$	Total charges of atoms in units of the proton charge						
				C <sub>1</sub>	N <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>
0	-39 217.84	10.25	5.16	0.135	-0.310	0.107	0.107	0.004	-0.022	-0.022
30	-39 214.72	10.25	5.12	0.135	-0.310	0.107	0.106	0.005	-0.021	-0.022
60	-39 212.92	10.28	5.10	0.133	-0.309	0.107	0.105	0.000	-0.021	-0.022
90	-39 212.94	10.34	5.11	0.131	-0.307	0.106	0.103	0.008	-0.020	-0.021
120	-39 214.76	10.41	5.14	0.128	-0.306	0.105	0.102	0.009	-0.019	-0.020
150	-39 217.91	10.47	5.18	0.126	-0.305	0.103	0.102	0.009	-0.018	-0.018
180	-39 221.51	10.51	5.22	0.125	-0.304	0.103	0.103	0.009	-0.018	-0.017
210	-39 224.60	10.51	5.26	0.125	-0.305	0.103	0.104	0.008	-0.018	-0.017
240	-39 226.36	10.48	5.28	0.127	-0.306	0.103	0.106	0.007	-0.019	-0.017
270	-39 229.34	10.42	5.28	0.129	-0.308	0.104	0.107	0.006	-0.020	-0.018
300	-39 224.54	10.35	5.25	0.131	-0.309	0.105	0.108	0.005	-0.021	-0.019
330	-39 221.43	10.29	5.21	0.134	-0.310	0.107	0.108	0.004	-0.021	-0.021

ever, does not correspond to the really most stable orientation of the methylamine molecule in the electric field, because the dipole moment does not lie in any of the planes formed by the axes of the coordinate system. In this molecule, the charge of the nitrogen atom is negative and the charge of the C<sub>1</sub>, H<sub>3</sub>, and H<sub>4</sub> atoms is positive. There is either a positive or negative charge on the H<sub>5</sub>, H<sub>6</sub>, and H<sub>7</sub> atoms depending on the orientation of the molecule and the field intensity. Methylamine in external electric field was also studied by Aleksankin and coworkers<sup>12</sup> using a modified INDO method. The effect of rotations is similar and present results can be considered qualitatively similar to those of Aleksankin. However, a quantitative comparison is not possible, because different approximations have been used.

### CONCLUSIONS

The results obviously show that the electrostatic field can influence the electronic structure of molecules and consequently their chemical and physical properties. Thus their behaviour in various chemical, biochemical, and physical systems (electrochemistry, mass spectroscopy, catalysis, structure of molecules in biological membranes, enzymatic processes, *etc.*) can be affected. The results point out the necessity of including into calculations the influence of environment – in this case of the electrostatic field – into modelling of such experimental conditions.

The results obtained in the MNDO approximation modified for inclusion of the effect of external electric field on selected molecules are in a qualitative agreement with results obtained by other methods of calculation. An exception is the ammonia molecule whose most stable orientation in external electric field worked out different from that obtained by Nakatsuji<sup>14</sup> in the *ab initio* calculations. The dominant source of differences is probably the MNDO approximation itself using a minimal basis set without polarization functions. The influence of the electric field on polarization of atomic orbitals<sup>16</sup> is also neglected. This effect can be taken into account either by using a larger basis of atomic orbitals depending on the external field intensity or by extending the basis set in general. In both cases, it is necessary to abandon the semiempirical MNDO parametrization and thus results incomparable with calculations for zero field can be obtained.

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Translated by P. Pracna.