ELECTRONIC STRUCTURE AND PROPERTIES
OF ALKOXYMETHYLENEMALONIC ACID DERIVATIVES

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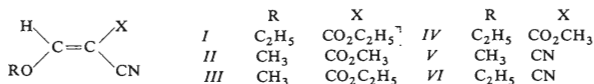
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Six compounds $RO(H)C=C(X)CN$ with $R = CH_3$ or C_2H_5 and $X = CO_2CH_3$, $CO_2C_2H_5$, or CN are characterized by some spectral data (IR, UV, ^1H-NMR — solvent effect). The PMR spectra did not confirm the presence of two geometrical isomers. Employing the quantum chemical calculations of the substance with $R = CH_3$ and $X = CO_2CH_3$ based on EHT, PPP, HMO, and CNDO/2, the geometrical isomerism is discussed in relation to the experimental dipole moments. The HMO indices of chemical reactivity agree with our present synthetic insight into nucleophilic substitution of the derivatives under study.

Substances of the alkoxymethylenemalonic type are frequently employed as the starting components for the ring formation during syntheses of heterocyclic compounds[1−3]. In the case of derivatives which do not contain the same substituents at the double bond (substances $I-IV$), the geometrical arrangement of the nitrile of carbalkoxy group with respect to the double bond plays an important role. The

	R	X		R	X
I	C_2H_5	$CO_2C_2H_5$	IV	C_2H_5	CO_2CH_3
II	CH_3	CO_2CH_3	V	CH_3	CN
III	CH_3	$CO_2C_2H_5$	VI	C_2H_5	CN

kind of the ring formed is often determined by the type of catalysis and the reaction conditions[4]. The geometrical isomerism of these derivatives and their analogues has been only little studied. Ceder and Stenhede[5] confirmed that the substance I can exist as two geometrical isomers, and studied the geometrical arrangement of the derivatives I, III, and IV by employing shift reagents. In the present work the conformation and configuration of the derivatives $I-VI$ is studied based on quantum chemical calculations applying the HMO, PPP, EHT, and CNDO/2 methods, compared with spectral data and dipole moments.

EXPERIMENTAL

The substances were synthetized by using the standard method (condensation of alkyl ortho-formate with the corresponding malonic acid derivative[6,7]). The characteristic melting points and the spectra are given in Table I. All the substances were purified by sublimation. The melting points have not been corrected.

The IR spectra were measured on a spectrophotometer Perkin–Elmer 325 in chloroform solutions, the UV spectra on an instrument Specord UV VIS (ethanol, concentration $0.5 \text{ mol} \cdot \text{l}^{-1}$), and the ^{1}H- and ^{13}C-NMR spectra on a spectrometer Varian XL-100 with the internal standard TMS and dioxane. Six solvents were used as follows: CCl_4, $CDCl_3$, acetone-d_6, benzene-d_6, nitrobenzene-d_5, and pyridine-d_5. The dipole moments were measured by employing the Halverstadt and Kumler method[8]. The quantum chemical calculations were performed by applying the standard HMO[9], PPP[10,11], Del Re[12], EHT[13], and CNDO/2[14] methods on computers Tesla 200, IBM-370, and Elliot 503.

Since the geometry of the derivatives under study has not been so far studied experimentally, we employed the standard tabulated values of the bond lengths and bond angles[15] for the study of the starting conformation. The parameters used are summarized in Table II.

Spectral Characteristics

The infrared spectra exhibit some characteristic bands. The methyl, methylene, and ethylene CH stretching vibrations appear at $2800 - 3000 \text{ cm}^{-1}$. A fairly constant

TABLE I

Some Physical Characteristics of the Compounds Studied

Sub-stance	M. p. °C	$\lambda_{max}{}^a$, nm $(\varepsilon \cdot 10^{-3})$	$\delta(CH_3)$	$\tilde{\nu}_{max}{}^b$, cm^{-1}			
				$\nu(C{=}O)$	$\nu(C{\equiv}N)$	$\nu(C{=}C)$	$\nu({=}COC)$
I	52—53	250·5 (14·9)	1 445 1 370	1 715	2 235	1 620	1 291 1 110
II	88—89	250·0^c (11·7)	1 445 1 365	1 723	2 230	1 620	1 260 1 118
III	97—99	250·0 (12·9)	1 445 1 370	1 715	2 230	1 625	1 260 1 115
IV	28	250·5 (11·5)	1 435 1 375	1 722	2 230	1 618	1 292 1 120
V	90—91	250·5^d (11·9)	1 445 —	—	2 218	1 618	1 285 1 155
VI	65—67	250·0	1 442	—	2 218	1 615	1 260 1 150

^{a} In ethanol; ^{b} in chloroform; ^{c} PPP calculation gave λ_{max} 246·6 nm; ^{d} PPP calculation gave λ_{max} 243·8 nm.

TABLE II

Parametrization of the Semiempirical Methods Used

All the data are given in eV or in the β-units.

Method	Quantity	Atomic centre				$(OCH_3)^a$
		C	H	N	O	
HMO[b]	$-h_i$	0·0	—	0·5	1·0	3·0
PPP	$-I_p$	11·6 (11·19)[c]	—	14·18	17·28	33·0
	$-A_p$	0·03 (0·10)[c]	—	1·66	3·7	11·47
	$-\beta$	2·388 (2·149)[c]	—	3·343	3·13	1·80
EHT	$-I_s$	21·01	13·6	26·92	36·07	—
	$-I_p$	11·27	—	14·42	18·53	—
	ξ	1·625	1·0	1·95	2·275	—
CNDO/2	$(I_s + A_s)/2$	14·051	7·176	19·316	25·39	—
	$(I_p + A_p)/2$	5·572	—	7·275	9·111	—
	$-\beta_A^0$	21·0	9·0	25·0	31·0	—

[a] Heteroatomic model; [b] for the resonance integrals, $k_{C \equiv N} = 1\cdot4$, $k_{C=O} = 2\cdot0$, $k_{O-C} = 0\cdot8$, for the other bonds $k_{ij} = 1\cdot0$; [c] for sp hybridization at the carbon.

TABLE III

Chemical Shifts in the ^{1}H-NMR Spectra of the Substances I—VI

For each substance, the first row pertains to solution in $CDCl_3$, the second to solution in benzene; all data in δ values relative to TMS.

Sub-stance	Substituent R			Substituent X			
	CH_3-	CH_3O-	$-CH_2O-$	CH_3-	CH_3O-	$-CH_2O-$	$=CH-$
I	1·56	—	4·38	1·33	—	4·28	8·04
	0·76		3·42	1·05		4·05	7·65
II	—	4·12	—	—	3·82	—	7·94
		3·36			2·88		7·28
III	—	4·14	—	1·32	—	4·26	7·98
		2·92		1·00		4·00	7·36
IV	1·46	—	4·41	—	3·81	—	8·08
	0·75		3·42		3·44		7·60
V	—	4·18	—	—	—	—	7·59
		2·72					5·87
VI	1·48	—	4·35	—	—	—	7·55
	0·45		2·91				7·16

frequency is exhibited by the nitrile CN stretching vibrations, $2235 - 2230 \text{ cm}^{-1}$; in the case of the compounds V and VI this vibration is 12 cm^{-1} shifted towards lower wavenumbers, which indicates a deeper delocalization of the system. The position of the $\nu(C{=}O)$ band is dependent on the alkoxy group bonded to it. The ethyl ester derivatives display this band 8 cm^{-1} shifted to lower wavenumbers as compared with the methyl ester derivatives. Another characteristic band typical of all the derivatives belongs to the $\nu(=C{-}O{-}C)$ vibration at 1250 cm^{-1}. The $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ bands can be identified at 1445 and 1370 cm^{-1}, respectively.

The UV spectra of the derivatives investigated show a symmetrical absorption band in the range near 250 nm (Table I), representing a typical $\pi \rightarrow \pi^*$ transition of the conjugated system. The effect of the alkyl group on the spectral patterns is negligible. The values of the molar absorptivity fall in the range $1 \cdot 2 - 1 \cdot 4 \cdot 10^4 \text{ l}$. $\text{mol}^{-1} . \text{cm}^{-1}$.

The characteristic signals in the ^{1}H-NMR spectra measured in $CDCl_3$ and C_6H_6, respectively, are given in Table III. In accordance with the work[5], the presence of two geometrical isomers could not be traced. The signal of the olefinic proton of the compounds $I-IV$ lies in the region $\delta\ 8 \cdot 08 - 7 \cdot 94$. The effect of the alkoxy group is such that the position of this signal for the methyl derivatives (III, II) is shifted towards higher magnetic field intensities as compared with the ethyl derivatives (I, IV); the methyl signal of the ester group is shifted analogously with respect to the methyl signal of the alkoxy group. The assignment of the signals to the individual alkyl groups (in the ester and alkoxy groupings), regarding their close similarity in the spectra, was based on the assumption that the contributions from the alkyls are

Table IV

Solvent Effect on the Chemical Shifts in the ^{1}H-NMR Spectra of the Substances I and III

All the data in δ units relative to TMS; proton designation: $CH_3^A{-}(CH_2^B)O{-}CH^C{=}C$, $CH_3^D{-}CH_2^E{-}OCO$.

Solvent	Substance I					Substance III			
	A	B	C	D	E	A	C	D	E
CCl_4	1·48	4·39	7·96	4·24	1·34	4·12	7·84	1·36	4·26
$CDCl_3$	1·46	4·38	8·04	4·27	1·33	4·14	7·98	1·32	4·26
$(CD_3)_2CO$	1·42	4·52	8·24	4·22	1·27	4·26	8·22	1·30	4·26
C_6D_6	0·75	3·42	7·65	4·05	1·05	2·92	7·36	1·00	4·00
$C_6D_5NO_2$	1·44	4·47	8·22	4·27	1·30	4·20	8·12	1·30	4·28
C_5D_5N	1·22	4·32	8·40	4·22	1·17	4·01	8·32	1·16	4·21

approximately additive and do not change appreciably on a change of the substituents in another part of the molecule. Furthermore, the solvent effect on the chemical shifts of the proton signals of the substances I and III was investigated. This effect obviously is not equal for the two alkyl substituents, which also facilitates the proton signal assignment to the individual groups. Anomalous chemical shifts as compared with the other solvents is found for the substances I and III in benzene (Table IV). It is likely that while the other solvents solvate first the sterically least hindered alkoxy group (different shifts for the ethyl groups in I, methyl groups in II), benzene forms probably the sandwich orientation with respect to the double bond (the ASIS effect). This can result in a large shielding of this bond and thus in a considerable shift of the olefinic proton signal towards higher field values. The interaction constant is 7·2 Hz for the substance I and 7·0 Hz for the substance III and is not influenced by the solvent.

The ^{13}C-NMR spectra were measured for the substances II and V. Their values along with the charges at the individual atoms are given in Table V. The compound V shows two nonequivalent nitrile groups, which is in agreement with the CNDO/2 calculation and is due to the different distances of these groups from the alkoxy group.

FIG. 1

The Assumed Sandwich Orientation of the Benzene Molecules with Respect to the Substance II
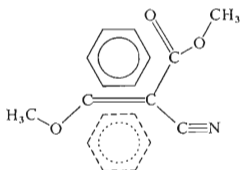
Quantum Chemical Calculations

As the starting model for the determination of the alkoxy group position with respect to the double bond plane served the dinitrile derivative V. This system possesses a smaller number of degrees of freedom and contains a smaller number of atoms than the ethyl derivative VI. The numbering in the two types of molecules in depicted in Fig. 2.

The total EHT energy of the molecule V decreases as the angle α increases (α is the dihedral angle between the planes formed by the atoms 1 C, 8 C, and 9 C, and 3 O, 4 C, and 5 H), which is due to the increasing distance of the methyl group from the double bond. The theoretical barrier of rotation of the methyl group in the methoxy grouping around the 1 C $-$ 3 O bond is 289·6 kJ/mol. In the region of $\alpha = 90-180°$ the energy curve exhibits a very broad minimum with the lowest point at $\alpha = 140°$

and with a very low transformation barrier 0·8 kJ/mol. This low barrier might permit free transformation of the methyl group above and below the plane of the conjugated system (deflection ±40°). The CNDO/2 calculation for this molecule gives the most favourable conformation for $\alpha = 180°$ with the value of the energy barrier 85·0 kJ/mol.

During the study of the conformation of the substance II, the rotations of the carbomethoxy group (angle β) and of the methoxy group in CO_2Me (angle γ) with respect to the double bond were regarded as well; the two conceivable geometrical isomers E and Z were considered, too. No allowance was made for the free rotation of the methyl group, since its energy barrier is extremely low.

From the energy dependences of the models, the E isomers emerge as preferred over the Z isomers in all the cases studied. Furthermore it can be stated that the s-*cis* arrangement of the C=C and C=O double bonds is the most favourable. The barrier of rotation of the carbomethoxy group is dependent on the orientation of the methyl in the alkoxy group and for the most favourable conformation it makes 30·1 kJ/mol. The rotational barrier for the methoxy group in CO_2Me calculated by the EHT method is considerable — 193·4 kJ/mol, which can be explained by the repulsion of the methyl group electrons and of the triple $C\equiv N$ bond π-electrons. On the other hand, the transformation barrier 1·3 kJ/mol probably allows a free oscillation of the methyl group in CO_2Me 60° over and under the plane of the π-conjugated skeleton. Fig. 3 shows the total energies of the E and Z isomers of the substance II in dependence on the angle β ($\alpha = 180°$, $\gamma = 0°$).

From the simplified EHT calculation it can be concluded that the most favourable from the energy aspect is the E isomer of the substance II, where the atoms 1 C, 3 O, 8 C, 9 C, 10 N, 12 O, and 13 O lie in a common plane. The methyl groups are tilted
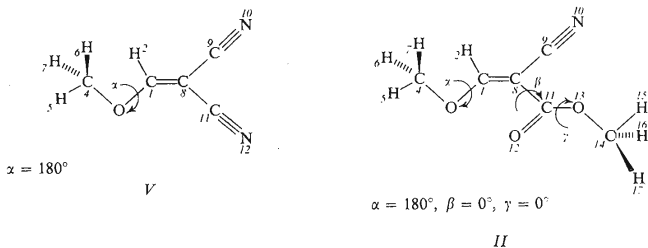

FIG. 2

Atom Numbering in the Studied Models of the Substances II and V

TABLE V

Comparison of the Calculated Atom Charges in the Substances *II* and *V* with the ^{13}C-NMR Chemical Shifts

For the atom numbering see Fig. 2.

| Atom A	Charge Q_A		EHT	CNDO/2	Shift δ_A
	Del Re + HMO	Del Re + SCF			
		Substance *II*			
1 C	0·277	0·167	0·719	0·225	176·11
3 O	--	--	−0·765	−0·182	--
4 C	--	--	0·400	0·131	52·62
8 C	−0·101	−0·081	−0·036	−0·097	86·11
9 C	0·308	0·318	0·799	0·105	113·49
10 N	−0·417	−0·367	−1·048	−0·157	--
11 C	0·397	0·407	1·359	0·406	164·40
12 O	−0·404	−0·464	−1·189	−0·335	--
13 O	--	--	−0·771	−0·230	--
14 C	--	--	0·400	0·402	64·92
		Substance *V*			
1 C	0·285	0·125	0·713	0·197	179·09
3 O	--	--	−0·786	−0·185	--
4 C	--	--	0·402	0·132	49·72
8 C	−0·134	−0·074	0·054	−0·268	65·95
9 C	0·307	0·317	0·814	0·098	111·19
10 N	−0·417	−0·367	−1·048	−0·157	--
12 N	−0·417	−0·367	−1·048	−0·157	--
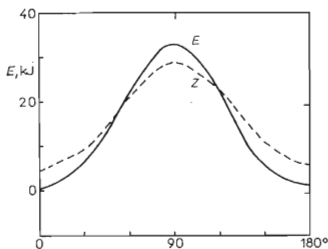
FIG. 3

The Total EHT Energy of the *E* and *Z* Isomers of the Substance *II* in Dependence on the Angle β

—— *E* isomer, ·········· *Z* isomer. $E_{totE} = -99029$ KJ, $E_{totZ} = -99024$ KJ.

from this plane by 60° (COOCH$_3$) and 30° (CH$_3$O) and owing to the low transformation barriers (less than 1·3 kJ/mol) they oscillate freely over and under this plane of the π-conjugated system. This is corroborated by the results of the paper[5], where the geometry described has been arrived at based on an interpretation of the NMR spectra.

The energy required for the isomerization of the substance V calculated by the EHT method is 128·1 kJ/mol. For the substance II this barrier is somewhat lower — 115·1 kJ/mol. These values are such that they do still allow the two isomers to be isolated, in accordance with the experiment[16] for alkylated analogues of the substances examined.

The classical PPP method was applied to the interpretation of the electronic spectra of the compounds II and V using the standard parameters (Table II). For the methoxy group the heteroatomic model was adopted. The total of nine monoexcited configurations were taken into account. The four possible geometrical isomers — the E and Z isomers with the two alternatives of the orientation of the C=O group with respect to the C=C bond — were considered. The best result, from the point of view of the longest-wavelength band, was obtained for those two derivatives possessing the s-cis arrangement of the C=C and C=O bonds in the molecule, the result being not very dependent on the configuration at the C=C bond. The longest-wavelength band is a so-called pure transition (type $1-1'$) whose configuration weight exceeds 97%.

We attempted to confirm the configuration at the double bond also by measuring the dipole moments of the substances II and V and comparing them with the values obtained from the CNDO/2 calculation. Fig. 4 shows the models investigated along with the μ values obtained. In the case of the compound V, the agreement with the experiment is better for the model Va than for Vb. The substance II was treated in the three most probable models $IIa-c$, of which the model IIb conformed best to the experimental value 4·09 D. This structure emerges as the preferred one also from the EHT calculation and interpretation of the NMR spectra; the s-cis arrangement of the C=C and C=O bonds complies with the PPP calculation.

Table V gives the charges at the atoms for the substances II and V pertaining to the preferred configurations, as calculated by the methods HMO + Del Re, PPP + + Del Re, EHT, and CNDO/2. The various charges are in a fair mutual agreement; only the EHT calculations gave appreciably different values, as expected, since they overestimate the charge distribution in the molecule particularly for the hetero atoms[17]. The C=C bond order is low due to the effect of the two nitrile groups. The electron deficits appear markedly at the atoms 1 C, 9 C, and 11 C̄; at the 8 C carbon atom an excess negative charge is found. A still higher polarization of the double bond occurs on replacing the nitrile group by a carbomethoxy group; a site with a pronounced electron deficit appears (the 11 C carbon atom in the carbonyl group)

as compared with the nitrile group carbon atom. The other electron charges are comparable with those in the compound *V*.

The HMO indices of chemical reactivity from the point of view of nucleophilic and electrophilic attacks were obtained. In Table VI are summarized the values of electron density Q, indices of free valency F, nucleophilic and electrophilic delocalizabilities S_n and S_e, and the corresponding localization energies L_n and L_e. The two compounds involve three nucleophilic centres, *viz.* the 1 C, 9 C, and 11 C carbons.
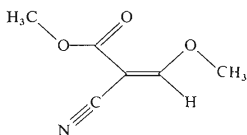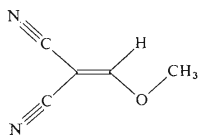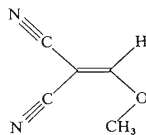

3.41D
IIa
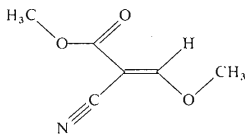
4.32D
IIb
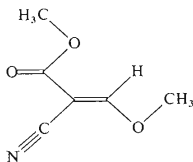
6.17D
IIc

5.20D
Va

2.6D
Vb

Fig. 4

Dipole Moments of the Substances *II* and *V* Calculated by the CNDO/2 Method

Experimental values: $\mu_{II} = 4{\cdot}09$ D, $\mu_V = 5{\cdot}85$ D.

TABLE VI
Some HMO Indices of Reactivity for the Substances *II* and *V*
  For the atom numbering see Fig. 2.

Position	q	F	S_n	L_n	S_e	L_e
			Substance *II*			
1 C	0·765	0·625	1·651	1·668	0·786	2·219
8 C	1·133	0·195	0·634	2·975	1·111	2·476
9 C	0·849	0·441	0·928	2·756	0·449	3·756
10 N	1·248	—	0·761	3·092	1·004	1·839
11 C	0·778	0·300	0·721	3·673	0·279	5·181
12 N	1·339	—	0·462	4·933	0·693	2·435
			Substance *V*			
1 C	0·765	0·643	1·740	1·623	0·843	2·121
8 C	1·118	0·160	0·618	3·047	1·092	2·548
9 C	0·849	0·446	0·931	2·747	0·452	3·747
10 N	1·244	—	0·759	3·100	1·001	1·848
11 C	0·849	0·446	0·931	2·747	0·452	3·747
12 O	1·244	—	0·759	3·100	1·001	1·848

According to the S_n and L_n indices, for both compounds studied the 1 C carbon is the most suitable for nucleophilic substitution, followed by the nitrile group carbon. For an electrophilic attack, the positions 8 C > 10 N > 12 O (substance *II*) and 8 C > 10 N = 12 N (substance *V*) are the most favourable.

The quantum chemical calculation confirmed the reactivity of the derivatives *II* and *V* toward nucleophilic reagents, which attack always the carbon 1 C; this has been found experimentally and confirmed by the isolation of some intermediate products of the anticipated type.

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