MOLECULAR STRUCTURE OF *para*-SUBSTITUTED 3-ARYL-2-ARYLMETHYLENE-3-OXOPROPANENITRILES IN SOLUTION PHASE

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The conformational structure of the title compounds has been investigated by application of EHT calculations, ^{1}H and ^{13}C NMR spectral measurements, and calculated/found electrical dipole moments. It has been proved that compounds *Ia—Ie* and *IIa—IIf* obtained by thermodynamical-ly-controlled Knoevenagel condensation are all *E* isomers. The dipole moment of compound *Ia* indicates a partially dipolar structure.

The 3-aryl-2-arylmethylene-3-oxopropanenitriles of the types *I—III* are useful precursors in syntheses of six-membered heterocyclic compounds *via* cyclocondensation reactions[1−6]. Therefore, for evaluation of the course of these reactions it is considerably important to have as complete information as possible about molecular structure of the unsaturated oxonitriles *I—III*, at least about the configuration of the exocyclic C=C bond. In spite of the fact that the compounds type *I* have been known for more than 60 years[7], the said basic configurational problem has not been convincingly solved yet. In the studies of cycloaddition reactions[8] and various spectra properties[9−12], the fragment —CH=C(CN)CO— was usually considered to have the *E* configuration, but the alternative *Z* has not been excluded either. Therefore, in this work we tried to verify the presumption mentioned[8−12] using considerations and experimental arguments concerning conformational behaviour of compounds *Ia—Ie* and *IIa—IIf*. Basic orientation in possible behaviour of the molecules studied was obtained by means of the EHT calculations, and these predictions were confronted with spectra characteristics and apparent electrical dipole moments in solution.

EXPERIMENTAL

The melting points were determined with a Boetius apparatus and are not corrected. The 3-aryl--2-arylmethylene-3-oxopropanenitriles *I* and *II* were prepared by the Knoevenagel condensation

of 3-aryl-3-oxopropanenitriles[13] with the respective benzaldehydes[7]. The yields obtained, the melting points and analytical data are given in Table I. The oxonitriles *III* are described in our previous paper[14]. All the EHT calculations were carried out by the standard procedure[15] using an ICL 4-72 computer and the parameters given in Table II. The non-diagonal elements of the *H*-matrix were calculated by Wolfsberg and Helmholtz approximation[16] with the empirical constant $K = 1.75$. The initial geometries of the MO models involved the ideal bond angles 120° or 180°, and the bond lengths were taken from the standard parameter set suggested in ref.[17].

TABLE I

p-Substituted 3-aryl-2-arylmethylene-3-oxopropanenitriles *I* and *II*

Compound	X	Y	Yield, %	M.p., °C	
				Found[a]	Literature date
Ia	$N(C_2H_5)_2$	H	70	92—94	89·0—93·0 (ref.[37])
Ib	CH_3	H	78	89—90	89·0—90·0 (ref.[36])
Ic	H	H	72	84—85	83·5—85·5 (ref.[36])
Id	Cl	H	59	101—103	102·0—103·8 (ref.[36])
Ie	NO_2	H	73	142—144[b]	143·0—144·5 (ref.[36])
IIa	$N(C_2H_5)_2$	CH_3	60	116—118	117·0—118·5 (ref.[35])
IIb	CH_3	CH_3	82	91—92	c
IIc	H	CH_3	73	97—98	95·0—96·0 (ref.[27])
IId	Cl	CH_3	57	98—100	d
IIe	NO_2	CH_3	61	154—156[b]	152·0—153·0 (ref.[27])
IIf	OCH_3	CH_3	85	95—96	94·0—96·0 (ref.[27])

[a] Crystallized from ethanol; [b] from benzene; [c] a new compound, for $C_{18}H_{15}NO$ (261.3) calculated 82·72% C, 5·80% H, 5·36% N; found: 82·86% C, 5·91% H, 5·29% N; [d] a new compound, for $C_{17}H_{12}ClNO$ (281·8) calculated: 72·46% C, 4·30% H, 12·58% Cl, 4·97% N; found: 72·66% C, 4·35% H, 12·68% Cl, 4·52% N.

TABLE II

Ionization potentials (I_{spd}, eV) and Slater exponents (S.E.) used in the EHT calculations

Atomic centre	$-I_s$	$-I_p$	$-I_d$	S.E.
H	13·600	—	—	1·300
C	21·400	11·400	—	1·625
N	26·000	13·400	—	1·950
O	32·300	14·800	—	2·275
Cl	25·267	13·688	3·980	2·033

The program used contains a part enabling automatic generation of the initial geometries by means of rotations and translations according to any arbitrary points in space or atoms in the molecule. The NMR spectra were measured with a Varian XL-100 (^{1}H) and a Tesla BS 567 apparatus with Fourier transformation (^{13}C) at 35°C (^{1}H) and 50°C (^{13}C) in deuteriochloroform with tetramethylsilane as the internal standard. The ^{13}C NMR spectra were measured with the proton wide-range decoupling and without decoupling with application of NOE at the working frequency of 25·14 MHz. The digital resolution of the decoupled spectra was 0·93 points per Hz, being 1·86 points per Hz with the spectra without the decoupling. The tilting angle was 30° in both the cases, and the pulse repetition time was 3—8 s. The dipole moments were determined from the dielectrical permittivities and the densities measured by the method of dilute solutions in the region of mass fractions from 10^{-2} to 10^{-4} in benzene at 25°C. The results were treated by the method of Halverstadt and Kumler[18]. The theoretical dipole moments considered for the individual configurations and conformations of the oxonitriles *Ia, Ic—Ie* and *IIa, IIc—IIe* were calculated from the bond moments and group moments according to the additive scheme[19]. The following moments were used involving, in all the cases, conjugation with benzene nucleus (in 10^{-30} Cm): C_{ar}—NO_2 13·34, C_{ar}—Cl 5·34, C_{ar}—H 0, C=O 8·34, μ_mCO 0·83 (ref.[20], the values used by the author), C≡N 13·01, C_{ar}—CH_3 1·33 (ref.[21]), and C_{ar}—$N(C_2H_5)_2$ 6·00 (ref.[22], the experimental value for N,N-diethylaminobenzene).

RESULTS AND DISCUSSION

EHT *Calculations*: Macroscopical models of compounds *I—III* indicate that the molecules cannot be planar due to numerous *ortho* interactions of the aromatic

(A)

(B)
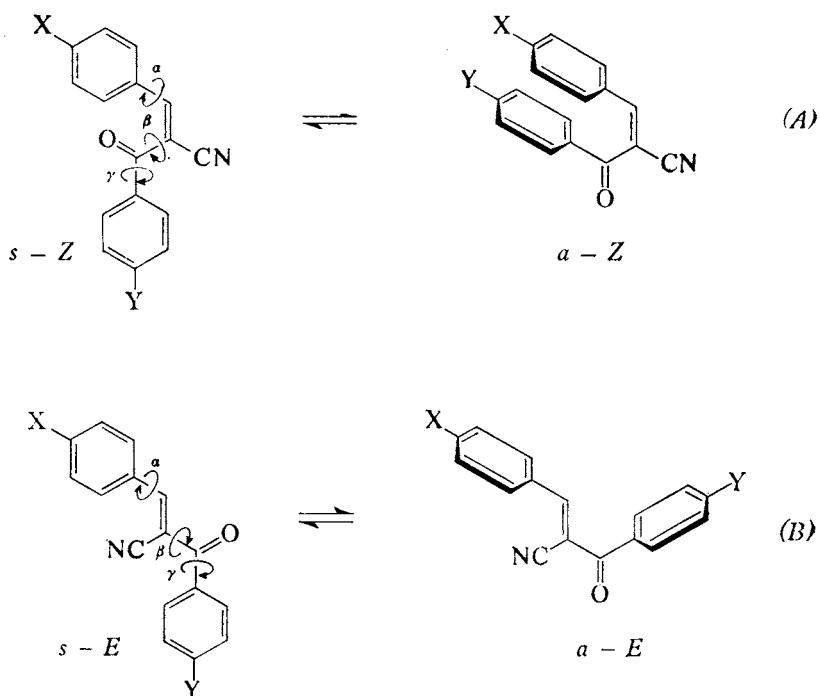
rings. Therefore, a real molecular structure must be, *a priori*, formulated by means of the states (not determined in any more detail in advance) situated geometrically between the pair of hypothetical planar structures with *syn* (*s*) or *anti* (*a*) orientation of the carbonyl $C=O$ with respect to the exocyclic $C=C$ bond. For the individual Z and E isomers it is then possible to write the equilibria (*A*) and (*B*) whose dynamics will probably be connected with smaller changes of the torsion angles α and γ but with a marked change of the torsion angle β. Under these presumptions, we tried to obtain an approximate picture of the most probable shapes of the molecules by studying the EHT energies calculated for the molecular models of the non-substituted compounds *I* in the rigid rotor approximation. The application of this simplified EHT approach to the said qualitative considerations is justified by its successful applications to medium-sized and large organic molecules (see *e.g.*[23-26]). In this way we tried to answer two basic questions: *1*. How many energetically advantageous conformational forms are to be taken into account in the two cases (*A*) and (*B*), and *2*. whether some of these forms exhibits such energetical stabilization that it could represent a justified reason for preference of the Z or E isomer of the oxonitrile *I*. The problem given was studied for the case of the parent oxonitrile *Ic* at first.

When solving the first of the above-mentioned questions, first we tried to estimate the less variable torsion angles α and γ. From dependences $E_{EHT} = f(\alpha)$ and $E_{EHT} = f(\gamma)$ given in Table III it is obvious that, for the Z isomer *Ic* in $s-Z$ conformation, we can most likely expect the torsion angles varying about the values $\alpha = 90°$ and $\gamma = 60°$ or $120°$. Moreover, if it is presumed that these torsion angles will not markedly change with the changes of the third torsion angle β, the β angle can be optimized at constant α and γ values to give an approximate picture of molecular shape of the respective Z isomer conformers of the *Ic* compounds. From Fig. 1, which summarizes this optimization in the form of the $E_{EHT} = f(\beta)$ curve for the case $\alpha = 90°$ and $\gamma = 60°$, it follows that the equilibrium (*A*) will be practically shifted to the left in favour of the $s-Z$ type conformers with the angle near to $40°$, because the corresponding energy minimum of the $a-Z$ conformer lies higher by $1\,040\ kJ\ mol^{-1}$. Analogous approach was applied to the E isomer *Ic*, and it gave the first estimates $\alpha \doteq 60°$ or $120°$ and $\gamma \doteq 60°$ or $120°$ (Table III). In the search for the optimum β values, four α and γ combinations could be considered out of which the representative case $\alpha = \gamma = 60°$ was investigated explicitly. From the $E_{ETH} = f(\beta)$ curve it is obvious that the E isomer of *Ic* can exist in two energetically close conformational forms, *viz.* $s-E$ and $a-E$, whose EHT energy difference is $9.45\ kJ\ mol^{-1}$ in the case concerned (Fig. 2). Consequently it can be predicted that the (*B*) equilibrium cannot be, *a priori*, considered to be shifted exclusively in favour of one of the conformational types, whereby, of course, it differs markedly from the equilibrium (*A*).

As far as the possible preference of one of the stereoisomeric forms E/Z is considered, the comparison of absolute E_{EHT} values of the minima at the $E_{EHT} = f(\beta)$ curves in Figs 1 and 2 shows that the lowest minimum for the $s-E$ conformation

TABLE III

The EHT relative energies of rotational conformers of E and Z isomers of the oxonitrile Ic and E isomer of the nitro derivative Ie, variation of the α and γ angles. The values are given in kJ mol^{-1}

Angle	s-Z (Ic)		s-E (Ic)		s-E (Ie)	
	α	γ	α	γ	α	γ
0	^{a}	118·0	173·0	112·0	184·0	111·0
10	^{a}	107·0	151·0	102·0	155·0	101·0
20	^{a}	63·7	91·9	60·8	95·9	60·3
30	542·0	27·5	41·2	25·9	44·3	25·6
40	234·0	8·1	13·3	7·4	15·6	7·5
50	96·3	1·2	2·5	0·7	4·0	0·8
60	39·9	0·1^b	0·0	0·0	0·3	0·0
70	14·5	1·1	0·4	1·3	0·0	1·3
80	3·5	2·2	1·3	2·4	0·6	2·8
90	0·0	2·5	2·0	2·5	0·8	2·6

^{a} The energy could not be calculated for the distances of the centres H—C$_{(5)}$ and oxygen of carbonyl group below 100 pm; ^{b} $E_{rel} = 0\cdot0$ for the angle 120°.

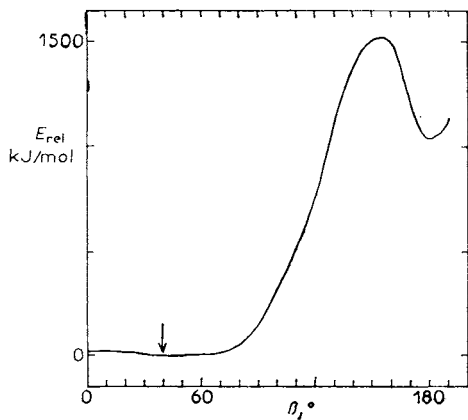FIG. 1

Dependence of relative EHT energies of Z isomer of the oxonitrile Ic on the torsion angle β
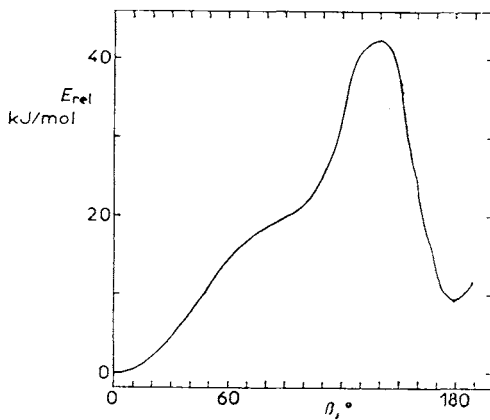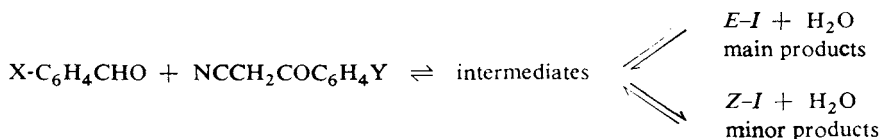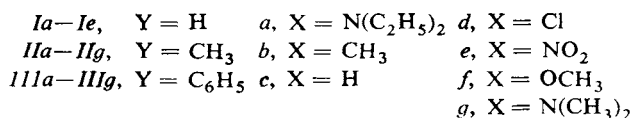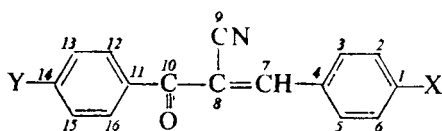

FIG. 2

Dependence of relative EHT energies of E isomer of Ic on the torsion angle β

lies lower than that for $s-Z$ by $21·6$ kJ mol^{-1}. This finding represents an argument in favour of energy stabilization of the E isomer of compound Ic, so that in accordance with the above-mentioned presumptions[8-12] it can be expected that the thermodynamically controlled Knoevenagel synthesis of compound Ic (according to the equilibria in Scheme 1, $X = Y = H$) will preferably give the Ic reaction product with E configuration. Further EHT calculations of the E isomer of the oxonitrile Ie showed that introduction of a nitro group did not substantially change the energy relations, as it follows from comparison of Figs 2 and 3. In the case of the chloro derivative Id (Fig. 4) and of the dimethylamino derivative Ig ($X = N(CH_3)_2$), which was taken a sa simpler model of the oxonitrile Ia, the $E_{EHT} = f(\beta)$ curves (Fig. 5) also show two minima for the conformers $s-E$ ($0°$) and $a-E$ ($160°$), the EHT energy difference between them being smaller than that of the oxonitriles Ic and Ie (Figs 2 and 3). In the case of the strongly electron-donor substituent p-$N(CH_3)_2$, the difference between the conformational forms $s-E$ and $a-E$ is only $1·6$ kJ mol^{-1}, hence the existence of the two forms could be equally probable.

$$Ia-Ie, \quad Y = H \qquad a, \ X = N(C_2H_5)_2 \quad d, \ X = Cl$$
$$IIa-IIg, \quad Y = CH_3 \qquad b, \ X = CH_3 \qquad e, \ X = NO_2$$
$$IIIa-IIIg, \quad Y = C_6H_5 \qquad c, \ X = H \qquad f, \ X = OCH_3$$
$$g, \ X = N(CH_3)_2$$

$$X\text{-}C_6H_4CHO + NCCH_2COC_6H_4Y \ \rightleftharpoons \ \text{intermediates}$$

$E\text{-}I + H_2O$
main products

$Z\text{-}I + H_2O$
minor products

SCHEME 1

The NMR *spectra* were chosen for evaluation of the E/Z configurational relations of the compounds $Ia-Ie$ and $IIa-IIf$, since a different spectral behaviour of the relatively short-living conformers cannot be expected with regard to the relaxation times. The ^1H NMR characteristics of the compounds type $I-III$ were only measured occasionally[10,14,27]. Therefore, we examined in detail the ^1H NMR spectra of the two series of derivatives $Ia-Ie$ and $IIa-IIf$ (Tables IV and V). From Table V it is obvious that the proton signal of the methine proton at 7 position (which is overlapped by the signals of aromatic protons) is only identified reliably in the series of the p-methyl derivatives $IIa-IIf$, where it exhibits minimum variability of the

chemical shift $(7 \cdot 93 - 8 \cdot 05 \text{ ppm})$. Application of the additivity rule[28] shows that these values are closer to the calculated proton shift in the E configuration $(8 \cdot 09 \text{ ppm})$ than to that of the Z configuration $(8 \cdot 12 \text{ ppm})$, but the differences are much too small to be significant. The ^{13}C NMR spectra of compounds $Ib-Ig$ and $IIIa-IIIg$ have already been investigated from the point of view of correlation of the chemical shifts of $C_{(7)}$ and $C_{(8)}$ atoms with the σ constants of the X substituents[12,14]. Table VI gives the spectral characteristics measured by us also for the series $IIa-IIf$, and these
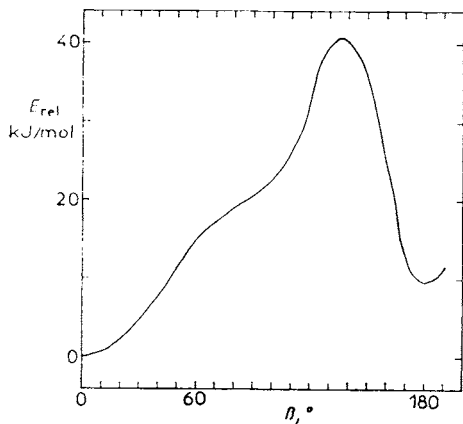

FIG. 3

Dependence of relative EHT energies of E isomer of Ie on the torsion angle β
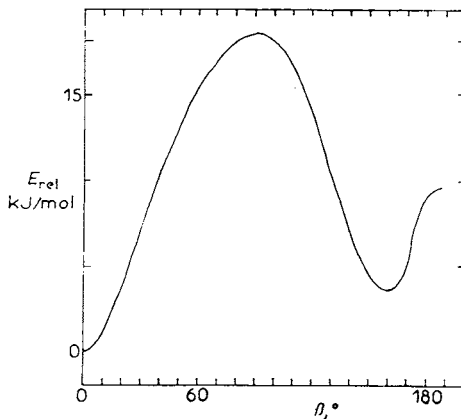
FIG. 4

Dependence of relative EHT energies of E isomer of the chloro derivative Id on the torsion angle β
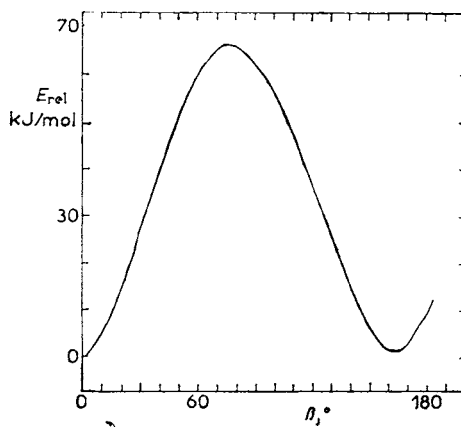
FIG. 5

Dependence of relative EHT energies of E isomer of the dimethylamino derivative Ig on the torsion angle β

values are very similar to the mentioned data[12] involving the *Ib−Ig* series, too, hence the following interpretation conclusions will obviously apply to both the series *I* and *II*. With regard to evaluation of the *E/Z* stereochemistry it is significant that the vicinal constants of spin–spin interaction $^3J_{\mathrm{CH}}$ in the —CH=C(CN)CO— (Table VII) are higher for the carbon nucleus of the cyano group (14·1 to 14·8 Hz) than for that of carbonyl group (5·6 to 6·1 Hz) with a smaller deviation in the case of the diethylamino derivative *IIa* (13·1 and 5·6 Hz). These findings correspond to the analogous constants measured *e.g.* for acrylic acid[29] for the mutual orientation of the hydrogen and carbon centres *E* (14·50 Hz) and *Z* (6·78 Hz). Hence it can be concluded that all the oxonitriles *IIb−IIf* and *Ib−Ie* have their exocyclic hydrogen

TABLE IV

^{1}H NMR spectra of the oxonitriles *I* (Y = H)

Compound	δ, ppm (C^2HCl_3, 35°C)^a
Ia	1·22 (t, 6 H, 2 × CH$_3$), 3·42 (q, 4 H, 2× CH$_2$), 6·63 (d, 2 H, H—C(2·6), *J* = 8·8 Hz), 7·38—8·08 (m, 8 H, H$_{arom}$ *a* = CH)
Ib	2·39 (s, 3 H, CH$_3$), 7·20 (d, 2 H, H—C(2,6), *J* = 8·8 Hz), 7·41 to 8·03 (m, 8 H, H$_{arom}$ *a* =CH)
Ic	7·38—8·10 (m, 11 H, H$_{arom}$ *a* =CH)
Id	7·40—8·10 (m, 10 H, H$_{arom}$ *a*=CH)
Ie	7·45—8·50 (m, 10 H, H$_{arom}$ *a*=CH)

^{a} Tetramethylsilane as the internal standard.

TABLE V

^{1}H NMR chemical shifts of the oxonitriles *II* (Y = CH$_3$). The values are given in ppm related to tetramethylsilane (C^2HCl_3, 35°C)

Compound	=C—H^a	H—C(2,6)^b	H—C(3,5)^b	H—C(12,16)^b	H—C(13,15)^b	CH$_3{}^a$	X
IIa	7·93	6·64	7·92	7·72	7·22	2·50	1·22 t 3·42 q
IIb	7·95	7·25	7·87	7·84	7·25	2·41	2·41 s
IIc	8·01	7·44—7·62^c	7·93—8·12^c	7·80	7·30	2·44	—
IId	7·97	7·45	7·95	7·79	7·29	2·44	---
IIe	8·05	8·32^d	8·12^d	7·83	7·33	2·45	—
IIf	7·98	6·98	8·02	7·77	7·27	2·42	3·87 s

^{a} Singlet; ^{b} doublet, *J* = 8·0 Hz; ^{c} multiplet; ^{d} *J* = 8·8 Hz.

centre at the E position and at the Z position with respect to the cyano and carbonyl groups, respectively, thus the configuration of the —CH=C(CN)CO— fragment really is E in all the cases examined. Using the published data[14], the same configuration assignment can be obtained also with the *p*-phenyl derivatives *III*. Some uncertainty remains with the *p*-dialkylamino derivatives (*e.g. Ia, Ig, IIa, IIIa,* and *IIIg*), some of whose ^{13}C NMR characteristics differ distinctly from the other derivatives of the respective series.
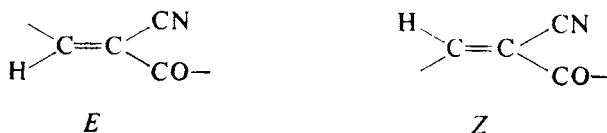
TABLE VI

^{13}C NMR chemical shifts of the oxonitriles *IIa, IIc—IIf.* The values are given in ppm related to tetramethylsilane (deuteriochloroform)

Carbon	*IIa*	*IIc*	*IId*	*IIe*	*IIf*
$C_{(1)}$	152·0	130·9	130·7	150·1	164·0
$C_{(2,6)}$	111·5	129·3	129·5	124·4	115·0
$C_{(3,5)}$	134·7	133·0	132·1	131·5	133·7
$C_{(4)}$	134·7	132·1	139·4	137·9	124·9
$C_{(7)}$	155·2	154·7	153·2	151·3	154·7
$C_{(8)}$	101·4	110·7	111·1	114·9	107·2
$C_{(11)}$	134·9	133·3	133·2	132·9	133·8
$C_{(12,16)}$	129·1	129·4	129·6	129·8	129·3
$C_{(13,15)}$	129·2	129·6	129·7	129·8	129·4
$C_{(14)}$	143·1	144·4	144·7	145·4	144·0
CH$_3$	21·6	21·6	21·7	21·7	21·6
X	44·9	—	—	—	55·7
	12·6				

TABLE VII

^{13}C NMR chemical shifts of C=N and C=O groups and the corresponding vicinal coupling constants $^3J_{HC=C-C}$ determined from the non-decoupled spectra of compounds *IIa, IIc—IIf*

Compound	$\delta(C{\equiv}N)$ ppm	$^3J_{HC=C-CN}$ Hz	$\delta(C{=}O)$ ppm	$^3J_{HC=C-CO}$ Hz
IIa	119·4	13·1	189·7	5·6
IIc	116·8	14·6	188·2	5·6
IId	116·8	14·1	187·9	6·1
IIe	116·2	14·1	187·2	6·1
IIf	117·7	14·8	188·8	6·0

$$\underset{H}{\overset{}{\diagdown}} C = C \underset{CO-}{\overset{CN}{\diagup}}$$

$$\underset{}{\overset{H}{\diagdown}} C = C \underset{CO-}{\overset{CN}{\diagup}}$$

E Z

Dipole moments. With these characteristics we can expect different sensitivity to both the E/Z configurational and $a-s$ conformational effects. Table VIII compares the dipole moments of benzenic solutions of oxonitriles $Ia-Ie$ and $IIa-IIe$ obtained from dielectrical measurements with those calculated by the additivity approximation[19] for the hypothetical planar forms in the equilibria (A) and (B). These theoretical values can be considered to be extreme limits between which the dipole moments of the non-completely planar molecular forms of compounds I and II can vary, and obviously they only depend on the change of substituent Y. Unambiguous assignment of the E configuration is only possible here for the p-nitro derivatives Ie and IIe along with the statement that in benzenic solutions they are present practically in the form of $s-E$ conformers (the differences between the calculated and found values are only 0·3 and 0·67 aCpm, respectively). With the Ic and IIc derivatives $(X = H)$ the found moments are rather close to the limit calculated value for the $a-E$ conformation, and with the p-chloro derivatives Id and IId they lie between the limit values for the $s-E$ and $a-E$ conformations. These findings can be summarized in the conclusion that increasing electronegativity of the Y substituent (in the order $NO_2 > Cl > H$) results in a shift of the conformational equilibrium (B) to the left. This presumption based on the conformational non--homogeneity of the oxonitriles $Ib-Ie$ and $IIb-IIe$ depending on the Y substituent was submitted to a verification test[30] consisting in plotting of the squares of the found dipole moments of the same skeleton with various substituents: if both the configuration and the conformation are identical, the experimental data lie on the calculated relations for the various torsion angles. In our case the problem was reduced to variation of the torsion angle β, because the calculated data are invariant with respect to changes of α and γ angles (the X and Y substituents are situated in the rotation axes). Figure 6 presents a typical case of the situations being verified for the pair of oxoderivatives IIc and IIe. Obviously, the experimental date does not lie on a straight line for any of the isomers Z or E, and the conformational homogeneity is not maintained here. Analogous results were obtained from comparisons of the other variations of the pairs of series $Ib-Ie$ and $IIb-IIe$.

$$\underset{C_2H_5}{\overset{C_2H_5}{\diagdown}} \overset{(+)}{N} = \underset{}{\underbrace{\hspace{1.5cm}}} = CH - C(CN) = \overset{\overset{(-)}{O}}{C} - \underset{}{\underbrace{\hspace{1.5cm}}} - Y$$
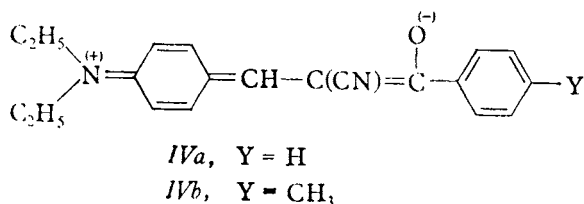
IVa,   Y = H
IVb,   Y = CH$_3$

TABLE VIII

Polarization and dipole moments of 3-aryl-2-arylmethylene-3-oxopropanenitriles *I* and *II* (benzene, 25°C)

Compound	$\mu_{\text{calculated}}$[a]				∞P_2, cm³ $R_D{}^b$	$\mu(5)^c$ $\mu(15)^c$
	s-Z	*a-Z*	*s-E*	*a-E*		
Ia	1·89	14·01	9·36	21·13	1 094·56	23·31
					89·36	23·18
Ic	4·32	19·40	4·32	19·40	450·87	14·38
					66·99	14·24
Id	1·30	14·58	8·74	20·85	393·94	13·14
					71·80	13·00
Ie	9·11	8·60	16·43	25·05	558·41	16·18
					72·67	16·08
IIa	3·05	15·17	9·66	22·43	979·97	21·88
					94·03	21·74
IIc	4·05	20·65	4·05	20·65	451·32	14·28
					71·64	14·14
IId	2·56	15·75	9·01	22·17	429·57	13·77
					76·45	13·61
IIe	9·93	9·39	16·89	26·35	652·95	17·61
					77·32	17·51

[a] The units used: 10^{-30} Cm; calculated from the bond and group moments (see Experimental);
[b] calculated from the individual increments according to Vogel[38]; [c] the 10^{-30} Cm units, correction for atomic polarization 5% or 15% of the molar refraction R_D.
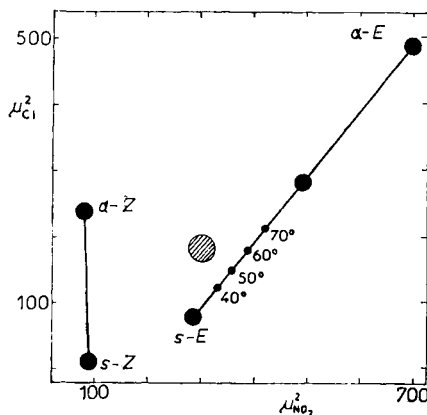

FIG. 6

Comparison of squares of dipole moments of oxonitriles *IId* (X = Cl, *y*-axis) and *IIe* (X = NO$_2$, *x*-axis). Full circles calculated for the individual conformations, dashed circle for the experimental value; full lines represent variation of the β angle for the *E* and *Z* configurations

The dipole moments of p-diethylamino derivatives Ia and IIa allow two alternative interpretations. The moment values found with these compounds are close to those calculated for the $a - E$ forms (differences -0.62 and 2.12 aCpm for IIa and Ia, resp.), hence the conformational equilibrium was shifted to the right, the relative energy preference of these conformers being also indicated by the EHT calculation of oxonitrile Ig (Fig. 5). The relatively high dipole moment value found with compound Ia, which is by 2.12 aCpm higher than the highest value predicted for the E isomer (the $a - E$ conformer), could be explained by the existence of the dipolar structure IVa, taking into account similar arguments as in the case of the E isomer of 3-(4-dimethylaminophenyl)-1-phenyl-2-propene-1-one and its vinylic analogues[31] and other strongly polar conjugated systems[32]. On the contrary, with the oxonitrile IIa the IVb structure will be less important due to negative effect of the electron-donor substituent Y $(Y = CH_3)$ at *para* position to carbonyl group, which corresponds to the dipole moments found for compounds Ia and IIa. Presumably, participation of dipolar structures IV will be more marked in more polar solvents than benzene, as it is the case with some analogues of 1,3-diphenyl-2-propene-1-ones[33]. The structures IVa, IVb can also explain the older findings[7,34,35] concerning deviations in chromophoric behaviour of compounds Ia and IIa in their electronic spectra. Correlations of wavenumbers $\tilde{v}(C=O)$ of IR spectra of the p-phenyl derivatives III with σ constants of the Y substituents and with the ^{13}C NMR chemical shifts show marked deviations from the regression line[14] just in cases of $N(C_2H_5)_2$ and $N(CH_3)_2$, which again can be explained by the $a - E$ conformation or by suppression of double bond character of $C=O$ in the molecules $IIIa$ and $IIIg$ and, hence, by lowering of the force constant of the corresponding vibration mode. Such behaviour was also observed with the simpler derivatives Ia and IIa.

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