DIPOLE MOMENTS AND CONFORMATION OF SOME OLEFINIC AND *ortho*-SUBSTITUTED AROMATIC METHOXY DERIVATIVES

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Dipole moments of stereoisomeric 3-methoxypropenenitriles (*I, II*), substituted 2-methoxybenzonitriles (*III— VI*) and substituted 2-chlorophenyl methyl ethers (*VII— X*) were measured in benzene solution and analyzed in terms of group moments. Aromatic derivatives *III— X* exist in the prevailing conformation *ap* (CH$_3$ *trans* to Cl or to CN). Any minor conformation was not detected; small differences between experimental and calculated dipole moments were explained by induction of the two adjacent dipoles. Conformations of 3-methoxypropenenitriles were estimated to prevailing *sp* for *I* and practically only *ap* for *II*. Irrespective of the conformations, dipole moments revealed a strong conjugation of the CN and OCH$_3$ groups in *I* and *II*. The intensity of this conjugation in various derivatives thus decreased steeply in the series: olefinic *E* > olefinic *Z* > aromatic *para* > aromatic *ortho*.

Configurations and equilibria of the olefinic derivatives XCH=CHY have been studied systematically[1−5] for variable substituents X and Y. A treatment by principal component analysis (PCA) revealed two main factors controlling the equilibrium of stereoisomers[5]: conjugation of unequal intensity in the two isomers and steric effect possible only in the Z isomer. The steric effect may be combined with short-range coulombic interactions, both repulsive and attractive, but a separation is difficult, particularly within the framework of PCA. When rotating groups are present, their effects are related to their conformation[4,6]. In particular the short-range effects are operative only in certain conformations and their possible effect on the E–Z equilibrium can be verified or disproved by determining their actual position[6,7]. Also in quantum chemical calculations of the $E \rightleftarrows Z$ equilibrium[4,7] the conformation must be determined simultaneously.

The object of the present paper are methoxy derivatives $(X = OCH_3)$ with a simple symmetrical group as the second substituent $(Y = Cl$ or $CN)$. The method of choice was dipole moment measurement in solution which allows to determine conformation rather reliably and also to get a semiquantitative information about

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the intensity of conjugation[8]. Measurements were carried out on the two stereo-isomers of 3-methoxypropenenitrile (*I* and *II*, Table I) and on 5-substituted 2-methoxybenzonitriles (*III* − *VI*), representing model compounds[6] for the sterically hindered *Z*-isomer. Additional substituents in *IV* − *VI* served to determine the direction of the experimental dipole moment which is not accessible directly[8]. In the case of methoxy--chloro derivatives the necessary 2-chlorovinyl methyl ethers have not yet been prepared in a pure state[9], hence our measurements were restricted to the aromatic models, 4-substituted 2-chlorophenyl methyl ethers *VII* − *X*. The conformation of *VII* and *IX* was already investigated[10−13] but comparison with substituted derivatives has been lacking.

III, R = H
IV, R = CH₃
V, R = Cl
VI, R = NO₂

VII, R = H
VIII, R = CH₃
IX, R = Cl
X, R = NO₂
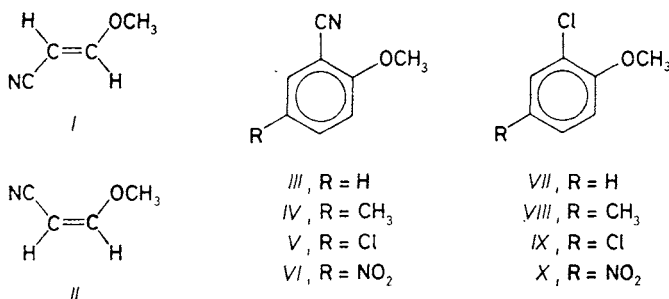
EXPERIMENTAL AND RESULTS

All the compounds *I* − *X* are known. To prepare *I* and *II* a slightly modified procedure[14] was used, their identity and purity was checked by ^{1}H NMR spectroscopy. Decisive for the configuration are the $^3J(H, H)$ coupling constants of the AB system, 13 Hz and 6·3 Hz for *I* and *II*, respectively. Identity and purity of *III* − *X* was based on their melting points, in some cases on the ^{1}H NMR and mass spectra.

For dipole moment measurements the same procedure was applied as previously[15], based on the Halverstadt–Kumler method[16]. As a rule five solutions of each compound were prepared in the range of weight fractions 0·0003 − 0·003. Molar refraction R_D was calculated from increments[17]. Correction for the atomic polarization was 5%.

Theoretical dipole moments (μ_{calc}) anticipated for individual conformations were calculated within the framework of bond and group moment scheme. The following standard values[8] were used for aromatic derivatives (in 10^{-30} C m): $H—C_{ar}$ 0, $C_{ar}—Cl$ 5·33, $C_{ar}—NO_2$ 13·33, $C_{ar}—CN$ 13·23, $CH_3—C_{ar}$ 1·0. The dipole moment of the methoxy group was expressed by a vector of 4·17 at an angle of 74° to the $C_{ar}—O$ bond[18]. All these values include a contribution from the conjugation with the benzene nucleus. When the groups OCH_3 and NO_2 are situated in the *para* position, their mutual conjugation was accounted for by an enhanced $C_{ar}—NO_2$ group moment of 16·1 as determined previously[18]. The group moments of substituents on an olefinic double bond are much less documented but seem to be generally

different from those on an aromatic system. For the compounds *I* and *II* we used the CN group moment of 11·80 derived from propenenitrile[19], and the OCH$_3$ group moment of 3·21 $\left(61° \text{ to the } C_{sp^2}\text{—O bond}\right)$ as determined on methoxyethene in the gas phase[20]. Hexagonal geometry was used for all aromatic derivatives. There are no X-ray data in the Cambridge Structural Database[21] on compounds with the groups OCH$_3$ and CN in the *ortho* position without further adjoining substituents, for the groups OCH$_3$ and Cl there are two examples but the angles C—C—Cl differ negligibly from 120°. The geometry of *I* and *II* was taken from the mono derivatives, methyl

TABLE I

Dipole moment data of some aromatic and olefinic methoxy derivatives (benzene, 25°C)

	Compound	α^a β^a	P_2^0, cm^3 R_D, cm^3	μ	$\mu_{calc}{}^b$
				10^{-30} C m
I	(*E*)-3-Methoxypropenenitrile	24·81 −0·121	413·2 21·7	14·6	*e*
II	(*Z*)-3-Methoxypropenenitrile	32·26 −0·150	529·1 21·7	16·6	*e*
III	2-Methoxybenzonitrile	20·90 −0·261	558·8 37·1	16·9	17·31 (16·80)
IV	2-Methoxy-5-methylbenzonitrile	19·22 −0·273	570·9 41·7	17·0	16·88 (17·20)
V	2-Methoxy-5-chlorobenzonitrile	14·07 −0·343	438·7 41·9	15·5	15·66 (15·60)
VI	2-Methoxy-5-nitrobenzonitrile	18·76 −0·367	670·2 43·4	18·5	17·57 (18·41)
VII	2-Chlorophenyl methyl ether	5·29 −0·373	174·9 37·4	8·7^c	9·43 (8·50)
VIII	2-Chloro-4-methylphenyl methyl ether	4·86 −0·337	181·0 42·1	8·7	9·07 (8·74)
IX	2,4-Dichlorophenyl methyl ether	4·99 −0·416	204·6 42·3	9·4^d	8·76 (9·13)
X	2-Chloro-4-nitrophenyl methyl ether	14·08 −0·497	533·8 43·8	16·4	15·01 (16·71)

^{a} Slopes of the plots ε_{12} vs w_2 and d_{12}^{-1} vs w_2, respectively; ^{b} calculated from standard group moments and standard geometry see Experimental (in parentheses, calculated from smoothed dipole moments of *III* and *VII*, respectively); ^{c} ref.[12] gives 8·2; ^{d} ref.[13] gives 9·2 and 9·3 at two different temperatures; ^{e} see formulae *Iap*, *Isp*.

vinyl ether[20] and propenenitrile[22], respectively: C=C—O 125° and C=C—CN 121°. The vector sum was calculated according to an algorithm in which every bond moment is decomposed into the three coordinates, the latter summed up separately and their vector sum gives the final result. The x-axis was chosen in the C—O bond.

DISCUSSION

Let us start the discussion with aromatic chloro-methoxy derivatives $VII - X$ since the results from dipole moments can be combined with those from other methods[10,11]. The direction of their dipole moments was determined by triangulation: the dipole moments of the substituted compound, of the unsubstituted compound and of the substituent itself are considered as three sides of a triangle. When the triangulation was repeated for the three substituents, CH_3, Cl and NO_2, good agreement was obtained (Fig. 1). The smothed moment of VII is represented by a vector of 8·5 (all dipole moments in 10^{-30} C m) at an angle of 79° to the C_{ar}—O bond. Experimental proofs in favour of a planar conformation of most aromatic methoxy derivatives were resumed[13,23]. Hence the dipole moment of VII can be interpreted in two ways: either by an equilibrium of the two planar conformers $VIIap$ and $VIIsp$, or by the single conformer $VIIap$, the deviation from the expected dipole moment being in this case assigned to conjugation or polarization. The expected dipole moments for $VIIap$ and $VIIsp$ were obtained by vector addition of the standard group moments (light arrows in Fig. 1), without any correction for the interaction of the two substituents. The result for $VIIap$ is much closer to the experiment as anticipated from the evident steric hindrance in $VIIsp$, but the divergence of 2·2 is well outside the error limits of the additivity principle. If we wanted to interpret the results in terms of the equilibrium $VIIap \rightleftarrows VIIsp$, the experimental dipole moments could be no longer treated as vectors but rather as scalar quantities, and the calculations should be done for each compound separately. For compounds VII and $VIII$ we obtained the population of the ap conformer 81% and 70%, respectively, but for IX and X there is no solution since either predicted value is lower than the experi-
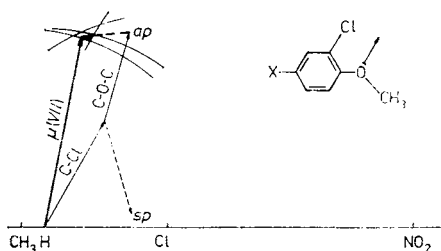

FIG. 1

Vector analysis of dipole moments of aromatic chloro-methoxy derivatives $VII - X$; full arrow — the smoothed dipole moment of VII; light and dotted arrows — group moments for the conformations ap and sp; broken arrow — difference between experimental and calculated dipole moments, expressing the effect of induction

mental value. For this reason and also with respect to the conclusions from far IR and ^{1}H NMR spectroscopies[10,11] we consider this explanation inacceptable and prefer the alternative with the equilibrium shifted practically toward *VIIap*. The same conclusion may be also drawn from comparison of calculated and experimental dipole moments in a simple plot[24] according to our well-tried method (not shown), this method is known[8] as insensitive to small discrepancies.

III ap, X = CN   *III sp*, X = CN
VII ap, X = Cl   *VII sp*, X = Cl
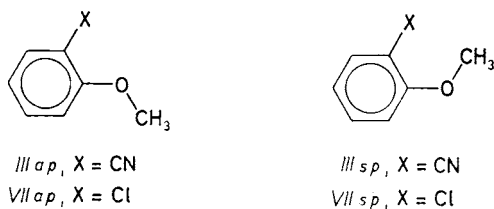
If *VIIap* is accepted as the single conformation present, the above mentioned difference must be explained as mutual electrostatic induction of the two dipoles C—O and C—Cl. Such effects are well known in other aromatic *ortho* derivatives[8] and are manifested e.g. in the lowered dipole moments of 1,2-dihalogenobenzenes[19]. If the difference is expressed as a vector, it is almost collinear to the O—C_{ar} bond (angle of 9°, broken arrow in Fig. 1). The induction seems to affect the C—O bond more than C—Cl, hence it may be also described as an increased conjugation of oxygen owing to the inductive effect of chlorine. Note still that angle deformations, although probable in ortho derivatives, cannot explain even a tenth of the observed effect.

When the above procedure was repeated with aromatic nitriles *III — VI*, very similar results were obtained. By triangulation we obtained the smoothed dipole moment of *III* as a vector of 16·8 at an angle of 68° to the C_{ar}—O bond, the fit is excellent (Fig. 2). An explanation in terms of the equilibrium *IIIap* ⇌ *IIIsp* would
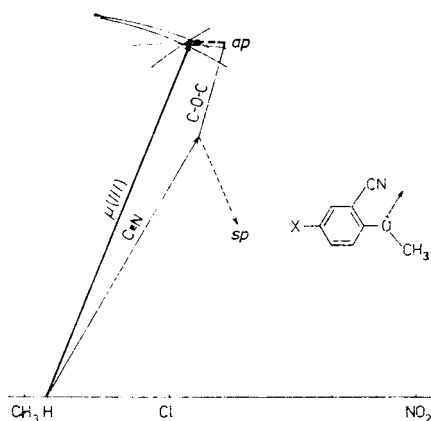

FIG. 2
Vector analysis of the dipole moments of methoxybenzonitriles *III — VI*; the same symbols are used as in Fig. 1

require populations of the *ap* isomers 88%, 81% and 96% for *III*, *IV* and *V*, respecti-
vely, but for *VI* there would be no solution. For this reason and for analogy grounds
we prefer again the explanation with the single form *VIIap*, the dipole moment
being lowered by induction. The latter effect is expressed as a vector, smaller than
in the preceding case (1·5) but of the same direction (8° to the O—C_{ar} bod). This
direction may mean either that the cyano group has a greater inductive effect on
the methoxy group than vice versa, or that the conjugation of the methoxy group
with the benzene ring is increased. The latter interpretation is less probable since
the effect is weaker in *III* than in *VII* and in 2-nitrophenyl methyl ether it is practically
zero[18]. On the other hand the induction may depend on the geometry in a less
evident way. The main problem is that the whole effect is relatively small and may
have several grounds. For this reason we have abandoned the attempts to estimate
the induction with reference to 1,2-dihalogenobenzenes and some kind of inter-
polation, although some semiquantitative predictions were attained.

I ap
μ_{calc} 10.4

I sp
μ_{calc} 10.8

II ap
μ_{calc} 15.0

II sp
μ_{calc} 10.2
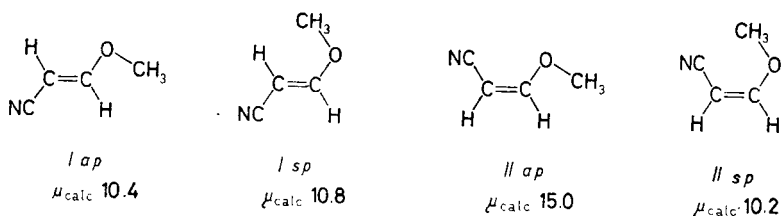
Summarizing, the conformation of aromatic methoxy derivatives *III − X* is known
in principle: the conformers *ap* are strongly prevailing or practically the only present.
The interaction of the two *ortho*-standing substituents is relatively weak and may be
understood in terms of mutual induction. Concerning the olefinic derivatives *I* and
II, the results are less definite for two reasons: firstly the direction of the experimental
dipole moment cannot be determined without additional substituents, secondly the
group moments used for olefinic derivatives (see Experimental) are less reliable.
With these group moments we calculated for the *E* isomer *I* in the conformations *Isp*
and *Iap* the dipole moments as given at the formulae. Since the experimental value
is distinctly larger, any decision about the conformation is not possible. The *sp*
conformation seems to be more probable in virtue of its preference in simple methoxy
ethene, investigated by several experimental methods[20,25 − 27] as well as by quantum
chemical calculations[28]. Assuming the conformation *Isp*, we get from the experi-
mental dipole moment a rather large contribution of 3·9, expressing the conjugation
of the two groups through the double bond. As expected, this value is larger than
the conjugation in 4-methoxybenzonitrile for which we get from the experimental
dipole moment[19] of 15·0 a value of 1·1.

The dipole moment of the *Z* isomer *II* is compatible only with the conformation
IIap. This is understandable with regard to the evident steric hindrance but a final

conformation is expected from an electron diffraction study[29]. The difference against the experimental value cannot be explained by induction as in the case of aromatic *ortho* derivatives *III — VI*: an additional vector in the direction from O toward C_{sp^2} would not improve the fit. The only explanation is again a conjugation of the two substituents through the double bond as in *I*. A vector oriented from O toward N can be estimated to 2·1. In conclusion the results are less dependable and less accurate than for aromatic derivatives, particularly the assumptions about the conformation need still to be confirmed. Nevertheless, it is evident that the conjugation is much more intensive in the *E* than in *Z* isomer; in this respect *para* aromatic derivatives are only a qualitative model for the *E* isomer and *ortho* derivatives cannot serve at all as a model for the *Z* isomer. Dependence of conjugation on the steric arrangement was observed even for other systems[30], the *trans* arrangement being more favourable (the stereoelectronic effect[31]).

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