

Dipole moments of some substituted benzaldehydes. Conformational preference of substituents ortho to the aldehyde group

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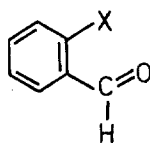
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Abstract. The dipole moments of a number of substituted benzaldehydes are measured in benzene solution. The angle which the dipole axis of the –CHO group makes with the axis of rotation of the group is determined. The observed moments of the ortho-substituted benzaldehydes are compared with the moments calculated for free rotation as well as for *s-trans* and *s-cis* orientations of the –CHO group. *o*-Fluorobenzaldehyde exists mostly in the *s-trans* conformation. *o*-Chloro-, *o*-bromo- and *o*-nitro-benzaldehydes also exist in the *s-trans* conformation; their observed dipole moments are even lower than the values calculated for *s-trans* forms, indicating mutual induction of the ortho substituents. Though 2,5-dichlorobenzaldehyde is expected to have the same dipole moment as benzaldehyde, the observed moment is significantly lower due to mutual induction of the ortho substituents. 2,5-Dimethylbenzaldehyde has, however, almost the same moment as benzaldehyde. The dipole moment of *o*-methoxybenzaldehyde is considerably higher than the values calculated for both *s-cis* and *s-trans* conformations. An explanation is given for this. *o*-Hydroxybenzaldehyde exists exclusively in the *s-cis* form due to internal H-bonding.

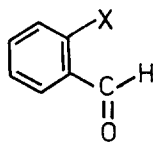
Keywords. Dipole moments of benzaldehydes; conformational preference of *o*-substituted benzaldehydes; dipole angle of –CHO group; mutual induction.

1. Introduction

An ortho-substituted benzaldehyde like **1** can exist in many conformations depending upon the angle which the plane of the –CHO group makes with the plane of the benzene ring. When the –CHO group is coplanar with the benzene ring, the molecule can have either *s-cis* conformation **1a** or the *s-trans* conformation **1b** (this nomenclature is based on the Kekule structure having a double bond between the carbon atoms to which the ortho substituents are attached) depending upon the nature of the substituent X.



1a



1b

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Though information on the conformational preference of the $-CHO$ group in mono-*o*-substituted benzaldehydes was obtained in the case of some aldehydes by NMR spectra (Wasylishen and Schaefer 1971; Schaefer *et al* 1980), IR spectra (Miller *et al* 1967) and INDO computations (Maciel *et al* 1970), such conformational studies need to be made for many other aldehydes. Dipole moment measurements can be a very useful means of obtaining conformational information on this type of molecules, especially when both the ortho substituents are polar in nature. This fact and the lack of information on the conformational preferences of many mono-*o*-substituted aldehydes prompted the present study. Schaefer *et al* (1980), who used NMR spectra and INDO molecular orbital calculations in their conformational studies of some substituted benzaldehydes, have indeed suggested dipole moment measurements as a good guide to conformations of molecules of this kind.

2. Experimental

2.1 Apparatus, measurements and calculation

The dielectric constants of the benzene solutions were measured with the apparatus described previously (Baliah and Ganapathy 1963). In the case of liquids the molar refraction (R_D) was calculated from the density and refractive index measurements. In the case of solids R_D was estimated from measurements made on benzene solutions with a Bellingham and Stanley refractometer of the Pulfrich type. Definitions of symbols and the method of calculating the dipole moments are given in an earlier paper (Baliah and Uma 1963).

2.2 Materials

The compounds available commercially were purified and used. The other compounds were prepared as described in the literature. They are listed in table 1 with their physical constants as found by us and also as given in the literature. The purity of all compounds was checked by g.l.c.

3. Results and discussion

The dipole moment data are given in table 2. In *o*-substituted benzaldehydes, whether or not there is inhibition of free rotation of groups can be determined by comparing the observed dipole moments with those calculated by vector addition of group moments assuming free rotation of the groups. When there is inhibition of free rotation, the observed moments should be significantly different from the calculated moments. Such a calculation requires a knowledge of the direction along which the moment of the $-CHO$ group acts with reference to its axis of rotation. Assuming the moments of $-CHO$ and $-Cl$ to be the same as the moments of benzaldehyde and chlorobenzene respectively, and using the moments of *p*-chlorobenzaldehyde (2.00 D), benzaldehyde (2.97 D) and chlorobenzene (1.57 D) (Baliah and Uma 1963) the angle which the moment of $-CHO$ makes with its axis of rotation (the axis being assumed to be directed towards the group) was found to be $38^\circ 38'$. A similar calculation was made from the moment of *p*-nitrobenzaldehyde (2.47 D), nitrobenzene (3.95 D) (Baliah and

Table 1. Physical constants of the aldehydes prepared.

Benzaldehyde	m.p. or b.p. (°C)		
	Present work	Literature values	Reference
<i>o</i> -Fluoro	m.p. 44–45	44.5	Clark 1957
<i>o</i> -Chloro	b.p. 212–13	213	Vogel 1954
<i>o</i> -Bromo	b.p. 229–30	118–19/12 mm	Angyal <i>et al</i> 1949
2,5-Dichloro	m.p. 57–58	58	DeCrauw 1931
2,5-Dimethyl	b.p. 67–68/4 mm	99–100/16 mm	Sato <i>et al</i> 1968

Table 2. Polarisation data of substituted benzaldehydes at 30°C.

Substituent(s)	α	β	P_2 (ml)	R_D (ml)	μ (D)	Literature value μ (D)
H	8.842	0.180	209.1	32.0	2.97	2.98 ^a
<i>o</i> -Methyl	6.572	0.180	197.9	36.7	2.83	
<i>p</i> -Methyl	9.441	0.139	251.8	37.0	3.27	3.24 ^b
<i>o</i> -Nitro	11.460	0.335	366.2	39.5	4.03	4.30 ^a
<i>o</i> -Chloro	7.018	0.338	221.7	36.9	3.03	
<i>p</i> -Chloro	3.122	0.315	118.4	38.2	2.00	2.05 ^c
<i>o</i> -Bromo	4.934	0.523	208.3	39.2	2.90	
<i>p</i> -Bromo	2.485	0.509	123.9	42.2	2.01	2.21 ^d
<i>o</i> -Fluoro	8.347	0.283	229.1	31.9	3.13	
<i>o</i> -Hydroxy	7.482	0.270	205.8	34.6	2.91	2.91 ^c
<i>o</i> -Methoxy	14.360	0.252	407.8	39.5	4.23	
2,5-Dichloro	4.545	0.385	191.2	42.9	2.71	
2,5-Dimethyl	7.278	0.144	221.0	40.6	2.99	

^aCalderbank and LeFevre 1949; ^bEstok and Dehn 1955; ^cCoomber and Partington 1938; ^dPearce and Berhenke 1935; ^eCurran 1945

Uma 1963) and benzaldehyde as well as from those of *p*-bromobenzaldehyde, bromobenzene (1.55 D) (Baliah and Uma 1963) and benzaldehyde, and the angles were found to be 38° 42' and 39°, respectively. Hence the angle was taken as 39°. The dipole moments of all the *o*-substituted benzaldehydes were then calculated, taking the group moments of –CH₃, –F, –OH, –OCH₃ and –COCH₃ as those of toluene (0.37 D) (Baker and Groves 1939), fluorobenzene (1.43 D), phenol (1.59 D), anisole (1.25 D) and acetophenone (2.90 D) (Baliah and Uma 1963). The angles which the moments of –OCH₃, –OH and –COCH₃ make with their axes of rotation (the axes being directed towards the group) are 105° (Baliah and Uma 1963), 92° (Baliah and Uma 1972) and 55° (Baliah and Aparajithan 1963), respectively. The calculated as well as the observed moments are given in table 3.

The observed moment of *o*-methylbenzaldehyde is almost the same as the moment calculated for free rotation, though it is slightly nearer to the *s-cis* conformation. The nearness is not significant considering its magnitude. Thus the dipole moment does not indicate preponderance of either of the conformers. This can be explained either on the basis of near-equal populations of planar *s-cis* and *s-trans* conformations or by assuming that the plane of the –CHO group in its mean position is almost

Table 3. Observed and calculated dipole moments of *o*-substituted benzaldehydes.

Substituent(s)	Observed μ (D)	Calculated μ (D) for		
		Free rotation	<i>s-cis</i> form	<i>s-trans</i> form
<i>o</i> -Methyl	2.83	2.85	2.63	3.05
<i>o</i> -Fluoro	3.13	3.76	4.34	3.09
<i>o</i> -Chloro	3.03	3.86	4.47	3.14
<i>o</i> -Bromo	2.90	3.85	4.45	3.13
<i>o</i> -Nitro	4.03	5.79	6.81	4.56
<i>o</i> -Hydroxy	2.91	3.15	2.89	3.40
<i>o</i> -Methoxy	4.23	3.10	2.93	3.27
2,5-Dichloro	2.71	2.97	2.97	2.97
2,5-Dimethyl	2.99	2.97	2.97	2.97

perpendicular to the plane of the benzene ring, its free rotation and planarity with the benzene ring being prevented by the *o*-methyl. The latter view is more probable. On the basis of long-range spin-spin coupling constants, the *s-cis* conformation is favoured over the *s-trans* by a free energy of 0.5 kJ/mol, the ratio of *s-cis* to *s-trans* being 55:45 in CCl₄ at 305 K (Schaefer *et al* 1980). In another investigation at a lower temperature of 128 K in CCl₂F₂/CHFCl₂ solution (Drakenberg *et al* 1975), the ratio was 50:50 as obtained from ¹³C NMR peak areas of the two conformers. Shift reagents added to a solution of the aldehyde in CCl₄ caused chemical shift dispersion interpretable as arising from a roughly 50:50 mixture of the two conformers (Grimand and Pfister-Guillouzo 1975). Therefore medium perturbations of the conformational equilibrium seem to be small. The *s-cis* population decreases only when the temperature is lowered. The ¹H NMR and ¹³C NMR data and the calculated (Lunazzi *et al* 1976; Drakenberg *et al* 1975) energy barrier of 28 kJ/mol to interconversion of the conformers led Schaefer *et al* (1980) to conclude that the aldehyde exists in planar *s-cis* and *s-trans* conformations in a 55:45 ratio at 305 K in CCl₄. Their conclusion is unlikely considering the bulkiness of the ortho substituents. The interpretation given by us from the observed dipole moment does not conflict with the recorded ¹H NMR and ¹³C NMR data. The extreme positions of the tilting -CHO impart to the molecule near but not planar *s-cis* and *s-trans* conformations.

The observed dipole moment of *o*-fluorobenzaldehyde is very close to that calculated for *s-trans* conformation. The *s-cis* conformation would be destabilised due to polar repulsive interactions of -CO and -F groups at close range. Wasylishen and Schaefer (1971) computed the *s-trans/s-cis* conformer ratio for *o*-fluorobenzaldehyde as 6:1 from the observed long-range couplings in the ¹H NMR spectra. The far-IR torsional data in the gas phase (Miller *et al* 1967) gave a ratio of 1.6 which differs markedly from the above one. The INDO computations (Maciel *et al* 1970) also showed the *s-trans* conformer to be more stable, the energy difference being 0.94 kcal/mol. In the light of the above findings, the study of the problem from the dipole moment point of view is of special interest. In fact, Wasylishen and Schaefer (1971) have suggested the determination of the dipole moment of this compound as a check on the conformational information reported by them. The observed dipole moment of 3.13 D in the present study indicates a very high predominance of the *s-trans* conformer -

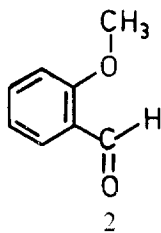
more than that reported by Wasylishen and Schaefer (1971) from NMR data. There is, however, one unknown factor in the estimation of the relative proportions of the two conformers from the observed dipole moment. The mutual induction of the ortho substituents lowers the dipole moment of the molecule (see the later discussion on *o*-chloro and *o*-bromo benzaldehydes). If the extent of this lowering by mutual induction can be estimated (which cannot be done at present) and if it is taken into account in the calculation, the *s-trans/s-cis* population ratio given by the dipole moment will actually be lower, perhaps comparing well with the ratio reported from ^1H NMR data. There is, however, no evidence that the predominant *s-trans* conformer is nonplanar (Bell *et al* 1969). If it is planar, the implication is that the *o*-fluorobenzaldehyde molecule exists almost exclusively in this conformation, which is what the dipole moment indicates.

The observed moments of *o*-chloro-, *o*-bromo- and *o*-nitro-benzaldehydes are less than the values calculated for both *s-cis* and *s-trans* conformations, though they are close to the *s-trans* values. The repulsive interaction between C=O and the ortho group is no doubt expected to destabilise the *s-cis* and favour the *s-trans* conformation but the observed dipole moments being lower than the values calculated for the *s-trans* forms is significant. In order to understand this ortho effect, we have to consider both steric repulsion and mutual induction. Since the calculated moments show that *s-trans* is the preferred conformation of the *o*-halogeno- and *o*-nitro-benzaldehydes with no nonbonded electron interactions, steric repulsion, which can widen the angle between the dipole axes, is not a factor to be reckoned with here. So the observed effect is presumably caused by mutual induction of the groups. Such is the case with a large number of ortho compounds like *o*-dihalogenobenzenes and *o*-nitrohalogenobenzenes; the observed moments are consistently lower than the calculated moments except when one dipole has its positive end towards the ring and the other its positive end away from the ring (Smyth 1955). For the compounds under consideration both the dipoles have their negative ends away from the ring.

2,5-Dichlorobenzaldehyde should have the same dipole moment as benzaldehyde if the C-Cl moments in the para positions cancel each other. But the dipole moment of 2,5-dichlorobenzaldehyde (2.71 D) is considerably lower than that of benzaldehyde (2.97 D). This is to be expected because the -Cl and -CHO, which are ortho to each other, have the negative ends of their dipoles directed away from the ring. Their dipole moments will be reduced by mutual induction. There will thus be a small moment acting along the C₂-C₅ axis. This, in combination with the reduced -CHO moment, accounts for the lower value observed for 2,5-dichlorobenzaldehyde. It is of interest to note that 2,5-dimethyl benzaldehyde and benzaldehyde have almost the same dipole moment (the moment of the former is higher only by 0.02 D). According to the generalisation made by Smallwood and Herzfeld (1930), mutual induction should raise the moment of 2,5-dimethylbenzaldehyde, the negative ends of the dipoles of the ortho -CH₃ and -CHO being directed in opposite directions. The methyl group has only a small dipole moment and the ortho effect here is apparently no larger than the experimental error. This may account for the very small increase observed.

In the case of *o*-methoxybenzaldehyde, *s-trans* is the favoured conformation because *s-cis* is destabilised by the repulsive interactions of the nonbonded electrons of the oxygen atoms. But the observed dipole moment (4.23 D) is much higher than the moments 3.27 D and 2.93 D calculated for the *s-trans* and *s-cis* conformations,

respectively. The methoxy group in *o*-substituted anisoles is known to assume an orientation in which the O-methyl is away from the ortho substituent (Dhmi and Stothers 1966; Schuster *et al* 1988). In the calculation of moments for the *s-cis* and *s-trans* conformation, free rotation of the molecule is assumed, if $\underline{2}$ is the conformation of the molecule without free rotation of the groups and if the dipole moment is



calculated for such a conformation, the value is 4.22 D which is remarkably close to the observed value of 4.23 D.

The observed dipole moment of *o*-hydroxybenzaldehyde is almost the same as the one calculated for the *s-cis* conformation. In this case the hydroxyl forms a strong intramolecular H-bond with the C=O of the formyl group, as indicated by IR spectra (Wulf *et al* 1936; Buswell *et al* 1937; Freymann 1938), reaction rate with phenylhydrazine and hydroxylamine (Vavon and Montheard 1940), viscosity and density (Pimental and McClellan 1960) and ^1H NMR (Dyer 1969). So the aldehyde exists wholly in the *s-cis* conformation.

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