# On the Extent of p-π-π Conjugation in Some β-Alkoxy-Substituted α,β-Unsaturated Ketones

ESKO TASKINEN

Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku, Finland

The electric dipole moments of some title compounds in benzene solution have been determined. By comparing the values of the experimental and estimated dipole moments it was found that the mesomeric p-π-π interaction in the $-O-C=C-C=O$ moieties of these compounds gives rise to mesomeric moments of 1.4—2.2 D. This fact, in comparison with the value of the mesomeric moment in simple alkyl vinyl ethers, shows that the carbonyl group of the title compounds has a marked conjugation enhancing effect on the parent $-O-C=C$ system.

It was previously shown[1] that in methyl vinyl ether the mesomeric p-π interaction in the vinyloxy moiety (1) leads to a mesomeric electric dipole moment (μ_m) of *ca.* 0.4 D,*

$$-O-C=C \leftrightarrow -\overset{+}{O}=C-\overset{-}{C} \tag{1}$$
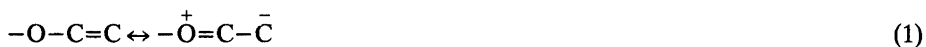
directed from the positively charged oxygen atom towards the negatively charged β carbon of the vinyl group. The mesomeric moment is defined by eqn. (2) where l stands for the distance between the charged of $+q$ and $-q$ on the oxygen and β carbon atoms,

$$\mu_m = q \cdot l \tag{2}$$

respectively. Since the value of μ_m is proportional to the distance between the charges, higher μ_m values are likely to be encountered in compounds with longer conjugated systems such as β-alkoxy-substituted α,β-unsaturated ketones where the p-π-π conjugation may be described by (3).

$$-O-C=C-C=O \leftrightarrow -\overset{+}{O}=C-C=C-\overset{-}{O} \tag{3}$$

In compounds with the alkoxy group *trans* to the carbonyl group, the distance between the opposite charges is about twice the corresponding distance in methyl vinyl ether. Since the value of μ_m is also proportional to the magnitude of q and hence to the extent ("strength") of conjugation, determination of μ_m values of these alkoxy-substituted

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* 1 D $= 3.33 \cdot 10^{-30}$ C m.

unsaturated ketones might give some information on the effect of the C=O group on the extent of conjugation in the vinyloxy group. In this work, attention is paid to the following compounds:

Dipole moment data for 2 and 3 were obtained from the literature;[2,3] experimental work on 1 and 4 is reported here.


RESULTS AND DISCUSSION

The molecular structure of 1 appears to be suitable for an essentially unhindered p-π-π conjugation: the MeO group is free to assume the energetically most favorable spatial orientation, i.e. the planar s-cis structure of methyl vinyl ether,[4] and the two π-systems are likely to be coplanar (the ring carbons, excluding C-5, probably lie in the same plane; cf. the structure of 2-cyclohexen-1-one[5]). The experimental μ value of 1, 3.74 D in benzene solution, is in satisfactory agreement with that for the corresponding 5,5-dimethyl derivative in CCl_4 solution (3.61 D[3]). To evaluate the magnitude of μ_m, the experimental μ value was compared with an estimated one, obtained by vector addition of the experimental dipole moments of appropriate, simple model compounds. Apparently, the approximate dipole moment of 1 may be considered to arise from a vector sum of the following dipole moments: (a) that of cyclohexanone (3.05 D, a mean of the values given in Ref. 6 for benzene solution), (b) that of dimethyl ether (1.35 D in benzene solution[7]), (c) that of cyclohexene (0.33 D in the gas phase,[6] the gas phase value being preferred because it is more accurately known than the solution value), and (d) the mesomeric moment μ_m. The mesomeric moment was assumed to be directed from the ethereal oxygen towards the carbonyl oxygen. By increasing the magnitude of μ_m until the vector sum of the contributing moments (a)-(d) matched the experimental μ value one arrived at μ_m=2.2 D.

1

2

3

4
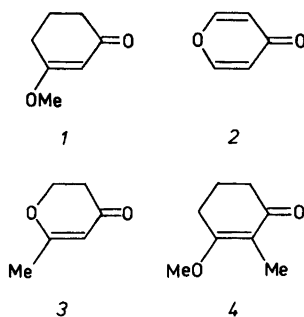
The magnitudes of μ_m in 2−4 were determined in a similar way. Because of molecular symmetry, the estimated dipole moment of 2 may be composed in a particularly simple way: the experimental dipole moment should be equal to a vector sum of the dipole moment of tetrahydropyran-4-one (μ=1.720 D in the gas phase[8]) and the mesomeric moment. This requires μ_m to be ca. 2.0 D since the experimental μ value is 3.72 D in benzene solution.[2] In a similar but assumingly less accurate way the dipole moment of 3 may be considered to arise from the following contributing moments: the dipole moments of tetrahydropyran-4-one and cyclohexene (1.720 and 0.33 D, respectively[6,8]), the induced moment due to the Me group (0.25 D[9]) and the mesomeric moment μ_m. The reported experimental μ value of 3.36 D in CCl_4 solution[3] leads to a μ_m value of ca. 1.4 D for 3.

In *4* the bulkiness of the Me group *cis* to the MeO moiety forces the latter to assume a non-s-*cis* conformation. Previous studies on related molecules show [10] that the trend towards a planar s-*trans* structure, where the conjugative interaction is most pronounced, is opposed by steric repulsions between the H atoms of the MeO group and the ring hydrogens *a* to the C=C bond. The high values of the mesomeric moment in *1–3*, however, suggest that despite these steric repulsions, a planar (or a nearly planar) s-*trans* structure might well be the most stable structure of *4*, owing to the strong stabilizing effect of the *p-π-π* conjugation in this spatial orientation of the MeO group. The validity of this idea may be tested by determining the value of μ_m in *4*. Following the procedure outlined above for *1–3*, the estimated dipole moment of *4* may be compiled from the dipole moments of cyclohexanone, cyclohexene and dimethyl ether, together with the inductive moment of the Me group bound to the C=C bond and the mesomeric moment. From the experimental dipole moment of *4* (4.94 D) the mesomeric moment is evaluated to be about 1.7 D. This value, calculated for a planar s-*trans* structure, is a minimum value of μ_m: if the MeO group of the actual molecule is tilted out of the planar s-*trans* structure, the mesomeric moment must have a higher value to satisfy the experimental μ value. However, it seems unlikely that the mesomeric moment would gain values higher than 1.7 D in any nonplanar structure of *4* in view of the μ_m value of 2.2 D for *1*. The high value of the mesomeric moment in *4* is in agreement with its high thermodynamic stability, relative to the β,γ isomer.[11]

It is interesting to note that the values of μ_m derived above for *1–4* (1.4–2.2 D) are roughly comparable with the magnitude of μ_m (2.5 D) in a structurally related enamino ketone of the type *5*.[12] This shows that the abilities of an alkoxy group and an amino group to conjugate with an adjacent unsaturated system are essentially equal. In view of the

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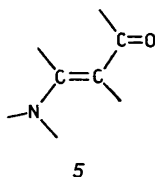
considerable values of the mesomeric moment in these compounds it is clear that when compiling the estimated dipole moment from contributing moments, μ_m can not be ignored (which occasionally has been the case[3]) unless it can be shown that the conjugative interaction is negligible.

When comparing the relative magnitudes of μ_m in *1–4* it should be taken into account that the distances between the ethereal and carbonyl oxygens in *2* and *3* are about 13 % shorter than those in *1* and *4* ($4.1 \cdot 10^{-10}$ m in *2* and *3*, $4.7 \cdot 10^{-10}$ m in *1* and *4*). To get an estimate of the relative extents of conjugative interaction in *1–4*, the μ_m values of *1* and *4* should thus be decreased by 13 % to obtain μ_m values comparable with those for *2* and *3*. Thus the "corrected" μ_m values for *1* and *4* are 1.9 and 1.5 D, respectively, to be compared with the actual μ_m values of 2.0 and 1.4 D for *2* and *3*, respectively. The relatively small range of these μ_m values, 1.4 to 2.0 D, thus suggests that the extents of conjugative *p-π-π* interaction in all these compounds are approximately equal.

From the distance between the two O atoms of *1* one may thus calculate that in *1* the magnitude of $|q|$ is *ca.* 0.10e⁻ (e⁻=the charge of an electron). For comparison, in methyl

vinyl ether the values of μ_m (0.4 D) and the distance between the O atom and the β carbon atom ($2.4 \cdot 10^{-10}$ m) lead to $|q|=0.04e^-$. Hence it may be inferred that the C=O group of *1* has a marked conjugation-enhancing effect on the $-O-C=C$ moiety.

Table 1. The values of α, β, $P_{2\infty}$, R_D^{20} and μ for *1* and *4*.

Compound	α	β	$P_{2\infty}/cm^3$	R_D^{20}/cm^3	μ/D
1	12.4	−0.236	325.6	33.6	3.74
4	19.5	−0.262	546.7	38.3	4.94

EXPERIMENTAL

The preparation of *1* and *4* has been described previously.[11] The dielectric constants were measured in benzene solution at 293.2 K. The μ values were calculated assuming $P_A=0.05$ P_E. For other details, see Ref. 9.

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