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DIPOLE MOMENTS OF SOME ALKYL VINYL AND ALKYL PROPENYL ETHERS

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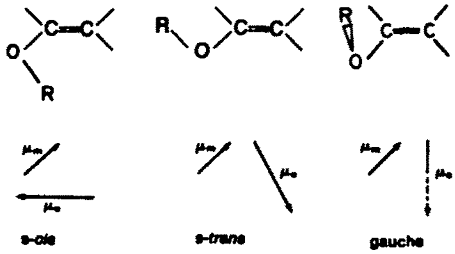
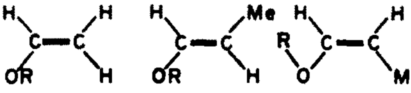
Abstract—Dipole moments of several alkyl vinyl and alkyl propenyl ethers have been determined by the Halverstadt-Kumler method in benzene solution at 293 K. The μ values depend on the bulkiness of the alkyl group present. In the alkyl vinyl ether series, a part of the varying μ values may be ascribed to changes in molecular geometry with varying bulkiness of the alkyl group. Other factors are clearly involved, since even in the alkyl (Z)-propenyl ether series μ values depend significantly on the alkyl group, although the geometry of the molecules remains essentially constant throughout the series. In the latter series, the total dipole moment is linearly related to the Taft's σ^*-values of the alkyl groups: $\mu/D = -(1.17 \pm 0.15)\sigma^* + (1.29 \pm 0.03)$. This suggests that the variation of μ with the alkyl radical follows from the changing polar character of the alkyl groups, which leads to changes in the value of the group moment μ_{RO}.

The dipole moments (μ) of dialkyl ethers are practically independent of the bulkiness of the alkyl groups: for example, $\mu = 1.35$ D for Me_2O, 1.29 *D* for Et_2O, 1.38 D for $i\text{-}Pr_2O$ and 1.29 D for $t\text{-}Bu_2O$ (benzene solution, 293 K).[1] On the other hand, the μ values of alkyl vinyl ethers $ROCH{=}CH_2$ are sensitive to the size of R: $\mu = 1.11$ D for R = Me, 1.19 D for R = Et, 1.48 D for R = i-Pr and 1.79 D for R = t-Bu (octane solution, 298 K).[2] Similarly, for the corresponding unsaturated thio ethers ($RSCH{=}CH_2$), μ depends considerably on the steric requirements of R: $\mu = 1.35$ D for R = Me, 1.47 D for R = Et, 1.58 D for R = i-Pr and 1.69 D for R = t-Bu (benzene solution, 298 K).[3] In the case of the unsaturated oxygen and thio ethers, a qualitative explanation of the variation of μ with the bulk of R follows directly from the changes in the conformations of the compounds in the same series: methyl vinyl ether prefers the planar s-*cis* configuration with respect to the O–C(sp^2) bond,[4] whereas t-butyl vinyl ether is likely to assume the planar (or nearly planar) s-*trans* configuration[5] (Trofimov *et al.*[3] suggest the non-planar *gauche* structure for this compound), and the other ethers with R larger than Me but smaller than t-Bu exist as mixtures of rotamers with considerable amounts of the two forms. Moreover, it is obvious that the main factors contributing to the total dipole moment are the moment (μ_e) due to the ether linkage (direction structure-dependent) and that (μ_m) due to the mesomeric interaction in the vinyloxy system ($-\underset{\cdot\cdot}{\ddot{O}}-C{=}C \leftrightarrow -\underset{\oplus}{\ddot{O}}{=}C-C{:}\ \ominus$), direction probably structure-independent, and hence structure-dependent changes in the orientation of μ_e lead to changes in the total μ values ($\mu_{tot} \cong \mu_e + \mu_m$). Attempts to correlate the experimental μ values with e.g. the hyperconjugative, steric and/or inductive constants of R in the series $RXCH{=}CH_2$ (X = O,S) have been made with some success,[2,3] but unfortunately the results do not reveal what fraction of the observed alteration in μ should be ascribed to the changes in the direction of μ_e and what fraction to the various (hyperconjugative, steric, inductive) properties of R. Because of the many contributing factors involved, correct interpretation of the experimental results is difficult and simplification of the systems investigated is necessary. This is the main object of the present work. The purpose was accomplished by studying the μ values of several alkyl (Z)-propenyl ethers (7–10) all of which assume the planar or nearly planar s-*trans* configuration about the O–C(sp^2) bond.[5] Accordingly, on going from R = Me to bulkier alkyl groups, the effect on μ of the changes in configuration is (at least largely) eliminated and any changes in μ should be ascribed to the varying electronic and steric properties of the alkyl groups involved. For additional information on related systems, compounds 1–6 were also included in the study.





1: R = Me
2: R = Et
3: R = i-Pr
4: R = t-Am

5: R = Me
6: R = t-Bu

7: R = Me
8: R = Et
9: R = i-Pr
10: R = t-Bu

RESULTS AND DISCUSSION

The experimental results are summarized in Table 1. In the alkyl (Z)-propenyl ether series (7–10), continuously increasing μ values are observed with increasing bulkiness of the alkyl group. On going from R = Me to R = t-Bu, the increase in μ (0.36 D) is, however, considerably smaller than that (0.82 D) in the alkyl vinyl ether series 1→4 [the t-Am (in 4) and t-Bu (in 10) groups are practically equivalent as to their effect on μ, *cf* Ref. 2]. A least-square treatment of the μ values of 7–10 against the Taft's σ^*-constants for the alkyl groups gives

$$\mu/D = -(1.17 \pm 0.15)\sigma^* + (1.29 \pm 0.03)$$

with a correlation coefficient of $r = 0.984$. Similarly, for the series 1–4 one obtains

$$\mu/D = -(2.7 \pm 0.5)\sigma^* + (0.97 \pm 0.09)$$

Table 1. Experimental values of α, β, $P_{2\infty}$, R_D^{20} and μ (benzene solution, 293 K)

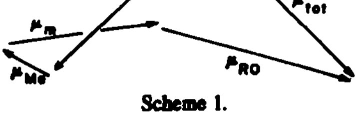
Compound	α	β	$P_{2\infty}/cm^3$	R_D^{20}/cm^3	μ/D
1[a]	0.73	−0.155	41.0	17.4	1.05
2	1.61	0.169	49.8	21.9	1.14
3	2.28	0.164	70.1	26.6	1.43
4	3.24	0.112	111.5	35.9	1.87
5[b]				21.9	1.23
6	1.76	0.345	88.1	35.9	1.56
7[b]				21.9	1.30
8	2.05	0.255	68.5	26.6	1.40
9	1.77	0.345	77.5	31.2	1.47
10	2.27	0.226	94.9	35.9	1.66

[a] At 298 K (Ref. 9). [b] From the following data: $\alpha = 2.19$, $\beta = 0.183$, $P_{2\infty} = 57.8$ cm^3 and $\bar{\mu} = 1.296$ D for a mixture of 92.7 % of **7** and 7.3 % of **5**; $\alpha = 2.00$, $\beta = 0.180$, $P_{2\infty} = 55.2$ cm^3 and $\bar{\mu} = 1.246$ D for a mixture of 19.7 % of **7** and 80.3 % of **5** ($\bar{\mu}^2 = v_1\mu_1^2 + v_2\mu_2^2$; v_1 and v_2 are the weight fractions of the two species).

with r = 0.973. In the latter case, μ can less precisely be defined by the constant σ^*, but inclusion of other (steric, hyperconjugative) parameters characteristic of R into the calculations has no real advantage, since it is obvious that expressing the μ values of alkyl vinyl ethers in terms of the various parameters mentioned is artificial and meaningless, unless one takes into account the changes with R in the relative directions of the components μ_e and μ_m, which exert the most important contributions to the total dipole moment. On the other hand, in the alkyl (Z)-propenyl ether series, such a treatment is more justified, because it appears that the geometry of the molecules remains essentially constant (i.e. the s-trans configuration prevails) throughout the series, irrespective of R.[5] It has been suggested, however, that especially t-Bu vinyl ether and hence, by analogy, t-Bu (Z)-propenyl ether should exist in the *gauche* form because of steric repulsion between the bulky t-Bu group and the α-H atom of the vinyl group in the planar s-*trans* structure.[2,6] Yet the experimental evidence for this view, based on the changes in the ^{13}C chemical shifts of the vinylic carbons in the alkyl vinyl ether series,[6] cannot be regarded as conclusive, since in the interpretation of the shift differences no attention was paid to the varying shielding effects of the alkyl groups on the shifts, which follow from the changes in molecular geometry and bulkiness of the alkyl groups in the series. This question is planned to be discussed in more detail in a later paper, but in this context it suffices to say that the experimental evidence available at present shows that a minor deviation from the planar s-*trans* configuration is possible for the t-Bu derivatives, but the dihedral angle about the O–C(sp^2) bond in the t-Bu–O–C=C system must be closer to 180° (s-*trans*) than to 90° (*gauche*).

In summary, it appears that no essential change in molecular geometry is involved on going from Me (Z)-propenyl ether to the t-Bu derivative. Against this background it is interesting to note the continuously increasing μ values in the series. In Scheme 1, the total dipole moment μ_{tot} of an alkyl (Z)-propenyl ether is represented as a vector sum of the most important bond and group moments, which are the following: (a) the bond moment of the O–C(sp^2) bond, (b) the inductive moment of the Me group,[7] (c) the mesomeric moment μ_m pointing approximately from the O atom to the β vinylic carbon, and (d) the moment of the RO group. It is seen that any change in the magnitude of μ_{RO} is reflected to an approximately equal extent in the magnitude of μ_{tot}, i.e. μ_{tot} should be a roughly linear function of μ_{RO}. Further, assuming that the magnitude of the latter is linearly dependent on the σ^* value of R (for comparison, $\mu/D = -1.416\sigma^* + 1.823$ for RCl in the vapor phase and $\mu/D = -2.200\sigma^* + 1.611$ for RI in CCl$_4$, Ref. 8), one arrives at the conclusion that μ_{tot} should be an approximately linear function of σ^*, in agreement with experimental results.

In the light of the significant changes in the μ_{RO} values in the alkyl (Z)-propenyl ether series, the essentially constant μ values of dialkyl ethers appear amazing, since they may be regarded as vector sums of two μ_{RO} values and hence they should depend considerably on R. The similar μ_{tot} values, however, do not prove that the groups moments μ_{RO} in dialkyl ethers are independent of R: in fact, $\mu_{t\text{-BuO}}$ has been estimated to be *ca.* 0.1 D higher than μ_{MeO}, but on going from Me$_2$O to t-Bu$_2$O, the increase in μ_{RO} is counterbalanced by widening of the R–O–R angle from 111° to *ca.* 120°.[1] The higher sensitivity of μ_{RO} in the alkyl (Z)-propenyl ether series



Scheme 1.

to changes in σ^* follows probably from the conjugation in the vinyloxy moiety, which effectively distributes the negative charge (donated by the alkyl group) from the O atom into the conjugated system. This effect is not possible in saturated ethers.

Vylegjanin *et al.*[10] have estimated the values of the dipole moments of the pure s-*cis* and the "less stable" (s-*trans*) rotamers of Me vinyl ether from the variation of μ_{tot} of the rotamer mixture with temperature:. μ = 0.80 D for the s-*cis* rotamer and μ = 1.72 D for the less stable rotamer (solvents: octane and cyclohexane). Using the experimental gas-phase μ value of 0.96 D for the s-*cis* rotamer of Me vinyl ether,[4] Aroney *et al.*[11] calculated a value of 1.48 D for the s-*trans* rotamer and a value of 1.25 D for the *gauche* rotamer with a dihedral angle of 90°. From the data of Table 1 the μ value of the *s*-trans rotamer of methyl vinyl ether may be estimated as follows. First, Me (Z)-propenyl ether **7** is likely to assume the same molecular geometry as the s-*trans* rotamer of Me vinyl ether. Thus the vector difference between the μ values of these compounds is equal to the inductive moment of the Me group (bound to the olefinic carbon) in **7**. The value of this inductive moment is obtained as 0.21 D from the difference in μ between **4** and **10**, both of which are likely to assume the same molecular geometry and which, moreover, have essentially equal alkyl groups as to their polar character. In addition, on the basis of some previous results,[7] the inductive moment of a Me group bound to an olefinic carbon is *ca.* 0.25 D with its direction roughly antiparallel with the μ_{tot} vector shown in Scheme 1. As an average, a correction of 0.23 D should be applied to the μ value of **7**, and hence μ = 1.53 D for the s-*trans* rotamer of Me vinyl ether. This is in good agreement with the value (1.48 D) calculated by Aroney *et al.*[11] for the s-*trans* rotamer, although they believed the second, less stable rotamer of Me vinyl ether to have the *gauche* form instead of the s-*trans*.

Similarly, the mutual agreement between the μ values of **1** and **5**, which are derived from different sources, may be checked by vector addition of the dipole moment of **1** (1.05 D) to that of a Me group, the angle between the vectors being *ca.* 40°.[7] Hence μ(calcd) = 1.26 D for **5**, in line with the experimental value of 1.23 D.

EXPERIMENTAL

Materials. Et vinyl ether **2** is commercially available; it was distilled prior to use. i-Pr vinyl ether **3** was prepared by transetherification[12,13] from i-PrOH and i-Bu vinyl ether, b.p. 330 K at 102.5 kPa. Similarly, t-Am vinyl ether **4** was prepared from **2** and t-AmOH, b.p. 373–375 K at 102.0 kPa. The preparation of **5**–**10** has been described previously.[5] The isomeric compounds were separated by preparative GLC using a Carbowax 20 M column. The purities of the compounds were checked by GLC and ^{1}H NMR spectroscopy.

Dipole moment determination. See Ref. 7.

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