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INDUCTIVE EFFECT OF SUBSTITUENTS ON THE DIPOLE MOMENT OF α-SUBSTITUTED VINYL METHYL ETHER

E. TASKINEN and E. KUKKAMÄKI
Department of Chemistry and Biochemistry, University of Turku, 20500 Turku 50, Finland

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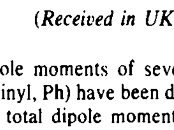
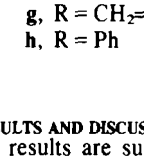
Abstract—Dipole moments of several α-substituted vinyl methyl ethers R(OMe)C:CH$_2$; R = Me, Et, i-Pr, t-Bu, cyclopropyl, vinyl, Ph) have been determined by the Halverstadt–Kumler method in benzene solution at 293 K. The square of the total dipole moment μ_R was found to be a linear function of the Taft's inductive constant σ_R^*: $\mu_R^2/D^2 = (0.619 \pm 0.033) + (1.092 \pm 0.10)\ \sigma_R^*$. The inductive contribution of the substituent R on the total dipole moment may be expressed by the equation $\mu_i/D = -0.52\,\sigma^* + 0.25$. This is in good agreement with the corresponding equation for the dipole moments of alkyl-substituted ethenes: $\mu_i/D = -0.58\,\sigma^* + 0.28$ (based on dipole moments obtained by PCILO calculations).

The dipole moment (μ) of ethene is expected to be zero on symmetry grounds, in agreement with experimental evidence.[1] On the other hand, propene has a permanent dipole moment of 0.364 D lying in the plane of the ethylenic system and forming an angle of 24.6° with the line passing through the olefinic carbons.[2] The direction of μ shows that an excess of negative charge is concentrated at the unsubstituted olefinic carbon. This effect may be interpreted to arise from the higher polar (electron releasing) character of the Me group, relative to that of an H atom. With more effective electron releasing (electropositive) substituents in place of the Me group, the μ values might be expected to be still higher. The corresponding ethyl derivative (1-butene) exists as an approximately 1:1 mixture of the s-*cis* and gauche rotamers[3-5] for which the μ values are 0.438 and 0.359 D, respectively.[4] Hence for the 1:1 mixture of the two rotamers $\bar{\mu} = 0.40$ D ($\bar{\mu}^2 = w_1\mu_1^2 + w_2\mu_2^2$, w_1 and w_2 being the weight fractions of the two forms). The dipole moment of 1-butene is thus higher than that of propene, as expected. In the absence of experimental dipole moment data for other, more electropositive alkyl derivatives (i-Pr, t-Bu) of ethene, a more thorough study of the relation between μ and the inductive character of the alkyl group is not possible.



Vinyl ethers are of great interest to us especially in view of their thermodynamic stability. Useful information on the properties of vinyl ethers might be obtained from a study of their dipole moments. Because of the presence of an olefinic linkage in vinyl ethers, the inductive effects of substituents on the total dipole moment can also be studied in substituted vinyl methyl ethers (**I**).



I

a, R = H
b, R = Me
c, R = Et
d, R = i-Pr
e, R = t-Bu
f, R = C_3H_5 (cyclopropyl)
g, R = CH_2=CH
h, R = Ph

RESULTS AND DISCUSSION

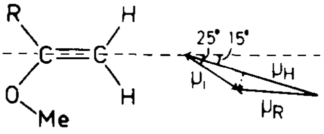
The experimental results are summarized in Table 1 together with corresponding literature data for the case R = H. The experimental μ values are treated as follows. First, according to the microwave studies of Cahill *et al.*[6] the total dipole moment (μ_H) of methyl vinyl ether

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
1a[a]	0.73	−0.155	41.0	17.5	1.05
1b	0.80	0.146	38.4	21.9	0.86
1c	0.33	0.191	39.5	26.6	0.75
1d[b]				31.2	0.57
1e	0.09	0.069	43.1	35.9	0.51
1f	0.55	0.007	43.6	29.8	0.77
1g	1.38	0.061	51.7	26.1	1.08
1h	1.10	−0.108	68.8	41.6	1.10

[a] At 298 K (Ref. 11). [b] From the following data: $\alpha = 0.21$, $\beta = 0.138$, $P_{2\infty} = 42.1$ cm^3 and $\bar{\mu} = 0.67$ D for a mixture of 92.4% of **1d** and 7.6% of its isomer, 2-Me-3-MeO-2-butene; $\alpha = 1.65$, $\beta = 0.122$, $P_{2\infty} = 68.5$ cm^3 and $\bar{\mu} = 1.31$ D for a mixture of 14.4% of **1d** and 85.6% of 2-Me-3-MeO-2-butene ($\bar{\mu}^2 = w_1\mu_1^2 + w_2\mu_2^2$; w_1 and w_2 are the weight fractions of the two species).

(R = H) makes an angle of *ca.* 15° with



the line connecting the two olefinic carbons. Second, the inductive moment (μ_I) of the group R is taken to lie in an angle of 25° with the C=C bond as in propene, and is assumed to be zero for R = H. Since the experimental dipole moment (μ_R) is a vector sum of μ_H and μ_I,

$$\mu_R^2 = (\mu_I \sin 10°)^2 + (\mu_H - \mu_I \cos 10°)^2.$$

Further

$$\mu_R^2 = \mu_I^2 + \mu_H^2 - 2\mu_I\mu_H \cos 10°$$

If $\mu_I < \mu_H$, then $\mu_I^2 \ll \mu_H^2$, and thus

$$\mu_R^2 \approx \mu_H^2 - 2\mu_I\mu_H \cos 10°.$$

If it is further assumed that μ_I depends linearly on the Taft's σ^*-value, one may write

$$\mu_I = \rho(\sigma_R^* - 0.49)$$

where ρ is a constant and 0.49 stands for the σ^* value of hydrogen. Hence

$$\mu_R^2 \approx \mu_H^2 - 2\mu_H \cos 10° \rho\, (\sigma_R^* - 0.49)$$

and

$$\mu_R^2 \approx a + b\, \sigma_R^*$$

where $a = \mu_H^2 + 0.98\mu_H \cos 10° \rho$ and $b = -2\mu_H \cos 10° \rho$. Thus μ_R^2 should be an approximately linear function of σ_R^*, in agreement with the experimental evidence shown in Fig. 1 (the σ^* values of the vinyl and cyclopropyl groups were taken from Refs. 7 and 8). A least-squares treatment of μ_R^2 against σ_R^* gives $\mu_R^2/D^2 = (0.619 \pm 0.033) + (1.092 \pm 0.10)\sigma_R^*$ with a correlation coefficient of 0.976. The smoothed value of μ_H^2 is obtained as 1.154 D^2 from the above equation by setting $\sigma_R^* = 0.49$. From the value of the slope of the line shown in Fig. 1 (= constant b) $\rho = -0.52$ and hence $\mu_I = -0.52\sigma_R^* + 0.25$ (D).

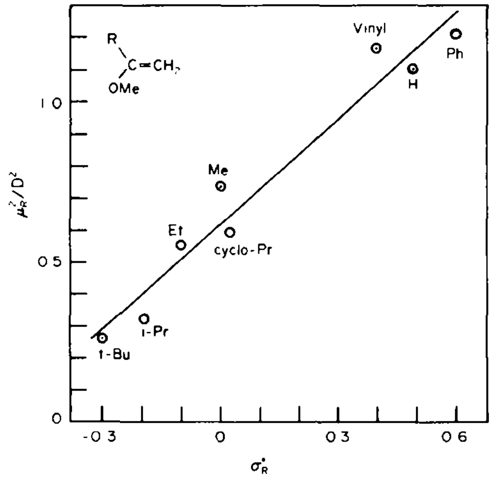


Fig. 1. The square of the total dipole moment of α-substituted vinyl methyl ethers as a function of the Taft's constant σ^*

As noted earlier, experimental μ data are available for the Me and Et but not for the i-Pr and t-Bu derivatives of ethene. However, Grignon and Fliszar[9] have calculated μ values for various alkyl-substituted ethenes, using the PCILO method: R = Me, μ = 0.24 D; R = Et, μ = 0.36 D; R = i-Pr, μ = 0.44 D; R = t-Bu, μ = 0.42 D. When these results are combined with the zero μ value for ethene, a least-squares treatment of μ_R against σ_R^* gives for the monoalkyl-substituted ethenes:

$$\mu_R = \mu_I = -0.58\,\sigma_R^* + 0.28\ (\mathrm{D})$$

with a correlation coefficient of 0.98. This equation resembles closely that derived experimentally for the inductive moment of substituents in α-substituted vinyl methyl ether.

In Ref. (10), several other examples of the correlations between μ_R and σ_R^* are cited. For example, $\mu_R = -0.444\sigma_R^* + 3.51$ (D) for alkyl cyanides RCN in benzene at 298 K.

EXPERIMENTAL

Materials. The syntheses of **1c**, **d** and **f** have been described previously.[12-14] Compounds **1b**, **e**, **g** and **h** were prepared from the corresponding ketones in an analogous manner. **1b**, b.p. 313 K at 101.8 kPa; **1e**, b.p. 368 K at 101.3 K; **1g**, b.p. 349 K at 101.3 kPa and **1h**, b.p. 357 K at 1.6 kPa. The purities of the compounds studied were at least 97%, as found by NMR and GLC.

Dipole moment determinations. The dipole moments were determined by the Halverstadt–Kumler method from dielectric constant and density measurements of dilute solns of the compounds in benzene at 293 K, following Exner.[15] The dielectric constants were determined by a WTW dipolemeter DM 01 equipped with a DFL 2 cell and the densities by a 5 cm^3 Sprengel–Ostwald pycnometer. The atomic polarization was assumed to be 5% of the electronic polarization calculated from the refraction equivalents reported by Vogel.[16]

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