

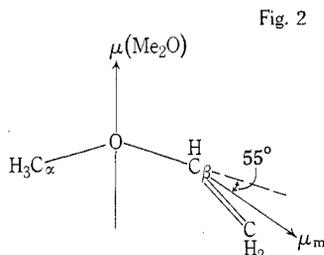
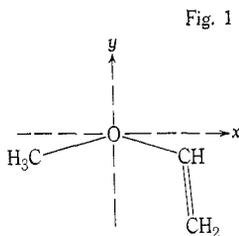
## SHORT COMMUNICATIONS

### CONFORMATIONAL ISOMERISM IN METHYL VINYL ETHER

By M. J. ARONEY,\* R. J. W. LE FÈVRE,\* G. L. D. RITCHIE,\* and J. D. SAXBY†

[Manuscript received March 11, 1969]

Cahill, Gold, and Owen<sup>1</sup> have recently examined the microwave spectrum of methyl vinyl ether and identified the more stable of the two rotational isomers as the planar *cis* conformation with a dipole moment in the ground vibrational state of  $0.96 \pm 0.02$  D, determined through the Stark effect. This moment is relevant to the interpretation of the Kerr constant of methyl vinyl ether in terms of the preferred molecular conformations. In our previous work,<sup>2</sup> molar Kerr constants were measured for methyl vinyl ether as a vapour and as a solute in carbon tetrachloride and benzene; the results were analysed assuming that both the *cis*-isomer and the other "unidentified" rotamer had a dipole moment of 1.10 D (the observed value in  $\text{CCl}_4$ ). The inadequacy of this assumption was pointed out. If, however, we use the newly reported moment of the *cis*-isomer, we are able greatly to extend our earlier conclusions and to specify the distribution of possible isomers using the experimental  $\mu$  and  $\infty_{(m)}K_2$  in carbon tetrachloride solution.



The observed polarity of the *cis* form of methyl vinyl ether ( $\mu_R = 0.96$  D) can be regarded as arising from a dimethyl ether moment (1.32 D in  $\text{CCl}_4$ )<sup>3</sup> acting in the  $y$  direction (Fig. 1), and a mesomeric moment  $\mu_m$  (having components  $\mu_x$  and  $\mu_y$ ) which results from interaction between the oxygen lone-pairs and the olefinic bond. Since  $\mu_R$  is directed virtually along the  $y$  axis (see Fig. 1 of ref.<sup>1</sup>) we deduce that  $\mu_x = c. 0$  and  $\mu_y = c. -0.36$  D. The latter term is a measure of the reduction through delocalization of the oxygen lone-pair moments. The dipole moment of any other conformer defined by the dihedral angle  $\phi$  between the  $\text{C}=\text{C}-\text{O}$  and  $\text{C}-\text{O}-\text{C}$  planes ( $\phi = 0^\circ$  for

\* School of Chemistry, University of Sydney, N.S.W. 2006.

† Coal Research Laboratory, Division of Mineral Chemistry, CSIRO, P.O. Box 175, Chatswood, N.S.W. 2067.

<sup>1</sup> Cahill, P., Gold, L. P., and Owen, N. L., *J. chem. Phys.*, 1968, **48**, 1620.

<sup>2</sup> Aroney, M. J., Le Fèvre, R. J. W., Ritchie, G. L. D., and Saxby, J. D., *Aust. J. Chem.*, 1967, **20**, 375.

<sup>3</sup> Aroney, M. J., Le Fèvre, R. J. W., and Saxby, J. D., *J. chem. Soc.*, 1962, 2886.

the *cis* form) may be calculated by vector addition of (a) an invariant dimethyl ether moment (1.32 D) located along the bisector of the angle COC, and (b) a mesomeric moment of magnitude 0.36 D which is taken as inclined at an angle COC/2 to the O-C<sub>β</sub> bond and which lies in the O-C=C plane (see Fig. 2). If the angle COC is taken as 110° as before,<sup>2</sup> calculated moments for various values of  $\phi$  may be obtained; these are listed in Table 1. Also included in this Table are the corresponding theoretical

TABLE I  
CALCULATED DIPOLE MOMENTS AND MOLAR KERR CONSTANTS FOR CONFORMATIONS OF METHYL VINYL ETHER

$\phi$	0°	30°	60°	90°	120°	150°	180°
$\mu$ (calc.) (D)	0.96	1.00	1.11	1.25	1.37	1.45	1.48
$10^{12} mK$ (calc.)	23.1	13.9	-5.5	-19.0	-17.9	-7.4	-1.5

$mK$  values derived<sup>4</sup> using these moments. The following additional data\* are required:  $b_L(C_\alpha-O) = 0.66$ ,  $b_T(C_\alpha-O) = b_V(C_\alpha-O) = 0.46$ ,  $b_L(C_\beta-O) = 1.77$ ,  $b_T(C_\beta-O) = b_V(C_\beta-O) = 0.46$ ,  $b_L(C=C) = 2.80$ ,  $b_T(C=C) = 0.73$ ,  $b_V(C=C) = 0.77$ ,  $\angle CCO = 120^\circ$ . Apart from the  $b_L(C-O)$  values the parameters are identical to those utilized in ref.<sup>2</sup> Estimates of the longitudinal polarizabilities for each C-O bond were obtained from the empirical rule of Le Fèvre<sup>5</sup> which relates  $b_L(C-O)$  with the internuclear distance  $r(C-O)$ ; the latter has values of 1.453 Å and 1.325 Å for C<sub>α</sub>-O and C<sub>β</sub>-O respectively.<sup>1</sup> The C-H bonds are regarded as isotropically polarizable with  $b_i = 0.65$ .<sup>6</sup>

The  $mK$ (calc.) values of Table 1 are significantly different from those quoted in ref.<sup>2</sup>, which were derived on the basis of an invariant  $\mu$  (1.10 D) acting along the COC bisector. If we now assume (as is indicated by infrared and microwave work<sup>1,7</sup>) that methyl vinyl ether exists as a mixture of two rotamers, one of which is the *cis* form, we are able to calculate the relative proportions of each isomer present for various dihedral angles  $\phi$  of the second isomer. Independent calculations are possible for both dipole moment and Kerr effect data using the following equations:

$$\mu_{\text{expt}}^2 = \mu_{cis}^2 x_{cis} + \mu_\phi^2 x_\phi \quad (1)$$

$$mK_{\text{expt}} = mK_{cis} x_{cis} + mK_\phi x_\phi \quad (2)$$

where  $\mu_{\text{expt}}$  and  $mK_{\text{expt}}$  are the measured values of the dipole moment and molar Kerr constant in CCl<sub>4</sub> solution;  $\mu_{cis}$  and  $mK_{cis}$  refer to the calculated parameters for the *cis*-isomer (Table I),  $\mu_\phi$  and  $mK_\phi$  relate to the second isomer (which is defined by  $\phi$ );  $x_{cis}$  and  $x_\phi$  are the mole fractions of the two conformers.

The results so obtained are shown graphically in Figure 3. Only when  $\phi$  is *c.* 90° do the dipole moment and molar Kerr constant curves predict a similar isomer

\* The polarizabilities of bonds  $b_L$ ,  $b_T$ , or  $b_V$  are quoted in Å<sup>3</sup> units throughout.

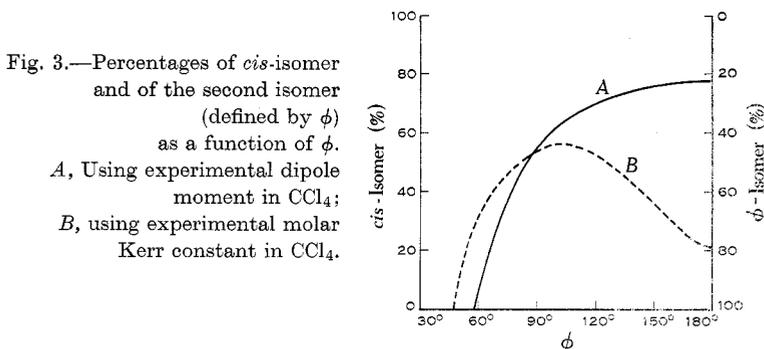
<sup>4</sup> Le Fèvre, R. J. W., *Adv. phys. org. Chem.*, 1965, **3**, 1.

<sup>5</sup> Le Fèvre, R. J. W., unpublished data.

<sup>6</sup> Le Fèvre, R. J. W., Orr, B. J., and Ritchie, G. L. D., *J. chem. Soc. (B)*, 1966, 273.

<sup>7</sup> Owen, N. L., and Sheppard, N., *Proc. chem. Soc.*, 1963, 264; *Trans. Faraday Soc.*, 1964, **60**, 634.

distribution. The existence of a *trans* or near-*trans* form appears to be precluded.<sup>8</sup> The possible error in  $\phi$  for the non-planar isomer may reasonably be estimated as  $\pm 20^\circ$ . This arises mainly from uncertainties in bond moments and polarizabilities and in the bond angles. Data obtained with benzene as solvent were not used in



these calculations since the molar Kerr constant exhibits a solvent dependence, i.e.  ${}_mK$  (in benzene)  $<$   ${}_mK$  (in CCl<sub>4</sub>).<sup>2</sup> Carbon tetrachloride may be regarded as an almost "inert" solvent whereas benzene is known to associate with ethers to form collision complexes through electrostatic interaction between the benzene  $\pi$ -system and the positive ends of localized dipoles within the solute molecule.<sup>9</sup>

If it is accepted that the second conformer has an approximately orthogonal structure we can calculate the energy difference  $\Delta E$  between the two isomeric forms (in CCl<sub>4</sub> solution) using equation (3):

$$x_{\text{orthog}}/x_{\text{cis}} = 2(f_{\text{orthog}}/f_{\text{cis}}) \exp(-\Delta E/kT) \quad (3)$$

where  $f_{\text{orthog}}$  and  $f_{\text{cis}}$  are the partition functions of the two conformations and the factor 2 accounts for the optical isomerism of the orthogonal rotamer.<sup>10</sup> Assuming the partition functions  $f_{\text{orthog}}$  and  $f_{\text{cis}}$  are equal, we calculate that  $\Delta E$  equals  $500 \pm 300$  cal/mole in CCl<sub>4</sub> solution (cf.  $660 \pm 200$  cal/mole found by Owen and Sheppard<sup>7</sup> for methyl vinyl ether in 1,1,2-trichloroethane).

<sup>8</sup> Hatada, K., Takeshita, M., and Yuki, H., *Tetrahedron Lett.*, 1968, 4621.

<sup>9</sup> Ledaal, T., *Tetrahedron Lett.*, 1968, 1683.

<sup>10</sup> Watanabe, I., Mizushima, S., and Morino, Y., *Sci. Pap. Inst. phys. chem. Res., Tokyo*, 1942, 39, 401.