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EVALUATION OF THE DIPOLE MOMENTS OF ETHOXYETHENE CONFORMATIONS

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The measured dipole moments (DM) of the most organic compounds are known to summarize the DM of every conformation. Though the DM values of the latter are a fundamental characteristic of molecule the problem of their estimation is still far from being solved.

Here a general evaluation procedure of the DM of the particular conformation is described with reference to ethoxyethene (CH_2=$CHOC_2H_5$). So long as this ether exists in two conformations[1,2] the net DM (μ_{eff}) is defined through the DM of the conformations (μ_1 and μ_2) as follows:

$$\mu^2_{eff} = N_1\ \mu^2_1 + N_2\ \mu^2_2 \qquad (1)$$

where N_1 and N_2 are the mole shares of the conformations in equilibrium. The conformation ratio at a certain temperature (T) depends upon the enthalpy difference (Δ H) according to the equation[2,3]:

$$N_1/N_2 = 2\ e^{-\Delta H/RT} \qquad (2)$$

Here the frequency factor 2 is intended to account for the entropy difference of the conformations since a "non-planar" one should be considered as having two "enantiomeric" forms (Δ S = Rln2). From Eqs. (1) and (2) with $N_1 + N_2 = 1$ one has:

$$\mu^2_{eff}\ (1 + 2e^{-\Delta H/RT}) = 2e^{-\Delta H/RT}\ \mu^2_1 + \mu^2_2 \qquad (3)$$

Thus, with ΔH known it is not difficult to calculate the μ_1 and μ_2 from the temperature dependence of μ_{eff}. On the other hand, if one puts any random number in the Eq.(3) instead the Δ H, then the experimental data will fit the Eq. (3) the better, the closer this number stands to the virtual Δ H quantity. Let us take the correlation coefficient (r) between $\mu^2_{eff}(1 + 2e^{-\Delta H/RT})$ and $2e^{-\Delta H/RT}$ as an accuracy criterion of the correlation and find the maximum of $r = f(\Delta H)$. Then ΔH_{max} value approximates the enthalpy difference of conformations.

The DM values of ethoxyethene measured in octane and cyclohexane solutions at various temperatures are listed in Table I.

Table I

The Temperature Dependence of the Dipole Moment of Ethoxyethene

T, °K	μ_{eff}, D	T, °K	μ_{eff}, D
227	1.10	298	1.20^x
227.5	1.10	298	1.20
239	1.12	298	1.17^x
250	1.15	303	1.18^x
262	1.14	303	1.17
285.5	1.14	308	1.19^x
288	1.17	308	1.22
290	1.19	308	1.18^x
293	1.18^x	313	1.19^x
293	1.18^x	318	1.24
298	1.19		

x) In cyclohexane.

Since both the octane and cyclohexane are of nearly equal solvation power and actually do not interact with the solute, one can consider the data from Table I as being the sample of the same parent population. These data have been processed via the computer after a special program to find the ΔH_{max} for the above stated correlation in the 650 - 2,500 cal/mole energy range. The procedure has been performed according to the Fibbonacci approach[4]. The results are the following:

$$\Delta H_{max} = 850 \text{ cal/mole}, \quad \mu_1 = 1.72 \text{ D}, \quad \mu_2 = 0.80 \text{ D}$$

The ΔH_{max} agrees well with the earlier independent estimations (800 - 1,200 cal/mole)[1-3,7] and therefore the estimated μ_1 and μ_2 values should be considered as being close to the proper ones.

The DM of alkoxyethene was found[5] to depend strongly on the alkoxy radical structure (contrary to the DM of saturated ethers which shows no significant variation with structure), e.g. for t-butoxyethene and methoxyethene the DMs are 1.84 D and 0.96 D, respectively. Taking into consideration that the former exists mainly as a non-planar conformation[6,7] while the latter occurs as a cis-planar form[7], it is reasonable to assign the 1.72 value to the non-planar conformation of ethoxyethene.

To check whether the data from Table I have sufficient variation to permit the use of this method we have carried out the above calculations for six μ'_{eff} sets which are defined for every T value from Table I as follows:

$$\mu'_{eff\ ij} = \mu_{eff\ i} + \gamma_j \delta \qquad (4)$$

where γ is the element of a random number set normally distributed about zero with variance 1 and δ is the measurement error of the DM taken to be 0.05 D[x].

Table 2

The ΔH, μ_1 and μ_2 values computed for the μ'_{eff} sets

ΔH, cal/mole	μ_1, D	μ_2, D	ΔH, cal/mole	μ_1, D	μ_2, D
		for $\delta = 0.02$			
802	1.69	0.79	802	1.30	0.91
777	1.58	0.89	826	1.47	1.04
787	1.48	0.94	826	1.77	0.72
		for $\delta = 0.05$			
787	2.07	0.34	814	1.88	0.54
777	1.73	0.78	830	1.39	1.02
826	1.59	0.91	874	1.48	0.94

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x) Virtually δ is about 0.02 - 0.03 D.

This procedure was used to simulate six independent experiments, each one giving the data set similar to that from Table I. The calculation results are given in Table 2. The following dispersions of ΔH, μ_1 and μ_2 have been computed using these data.

	$\sigma_{\Delta H}$	σ_{μ_1}	σ_{μ_2}
for $\delta = 0.02$	20	0.17	0.11
for $\delta = 0.05$	35	0.25	0.23

Therefore, the data from Table I may be considered sufficient to estimate the DM of ethoxyethene conformations.

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