Dipole Moments and Internal Rotation in Some Substituted Hydrocarbons

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Letter to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

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IT has long been recognized that one of the best methods of studying internal rotation is by means of the variation of dipole moments with temperature. However, this is applicable only to molecules having dipoles on each of the internally rotating groups; moreover, for vapor measurements, the compounds must be stable over relatively large ranges of temperature. Solution measurements of dipole moment *vs.* temperature are of interest and have been carried out,[1] but the evaluation of the internal rotation is vitiated by our lack of knowledge as to the effect of the solvent on the measured dipole moment.

The dipole moment method applied to such molecules in the vapor state is unique among means of investigating internal rotation in that it yields an isolated quantity which is a direct function of the rotation. This is in contrast to the thermodynamic method, the results of which depend on the small difference between two large numbers, and to the method of electron diffraction, in which the resulting pattern is a function of much more than the parameters pertaining to the internal rotation. Since only

TABLE I.

Molecule	Temp. range, °C	Moment $\times 10^{18}$	V_0 cal./mole
1,2-dichloropropane	70–235	1.45–1.68	2500
2,3-dichloropropene	125–245	1.74–1.77	2075
1,1,2-trichloroethane*	105–258	1.45–1.47	2820
1,3-dichloropropene			
104° isomer	120–208	1.78	—
112° isomer	120–230	1.81	—
1,4-dichlorobutane	160–235	2.22	—

* This compound displays a flat though definite minimum of 1.40 at 170°.

relatively little experimental data on vapor measurements of moment *vs.* temperature exist in the literature,[2] it was considered worth while to investigate other cases of interest with respect to internal rotation.

Table I presents a brief resume of our measurements to date. By far the most interesting result is that for 1,1,2-trichloroethane, for which the moment first decreases then increases with temperature; this behavior is in qualitative agreement with the electron diffraction results of Turkevich and Beach.[3] As a preliminary analysis, the potential energy barrier V_0 has been calculated for several of the compounds by the method of Beach and Stevenson,[4] who apply the function

$$V(\varphi) = (V_0/2)(1 - \cos \varphi)$$

to the internal rotation; in these calculations we have used 1.85 as the group moment of CH_2Cl.

A complete description and fuller analysis is in process of preparation.

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