# *Dipole Moment and Internal Rotation of 1, 4-Dichloro-2-butyne in the gaseous State*

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The dipole moment of 1, 4-dichloro-2-butyne in carbon tetrachloride and benzene solutions was previously reported by us[1], and the report showed a slight increase with temperature, causing the hindering potential of 700 cal./mole. Since the solvent exerts considerable influence upon the hindering potential of the internal rotation[2], it is desirable to measure the dipole moment in the vapor state to evaluate the hindering potential of the free molecule. The sample was prepared from 2-butyne-1, 4-diol according to the method of Johnson[3], b. p., 66–68°C/17 mmHg. The apparatus used is the one described already[4]. The result of the measurement is given in Table I. The moment is found to be constant through the whole range of temperature of the measurement, contrary to the

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[1] Y. Morino, I. Miyagawa and A. Wada, *J. Chem. Phys.*, **20**, 1976 (1952).

[2] S. Mizushima, Y. Morino and K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **25**, 159 (1934).

[3] A. W. Johnson, *J. Chem. Soc.*, **1946**, 1009.

[4] T. Chiba, This Bulletin, **28**, 19 (1955).

TABLE I

THE OBSERVED POLARIZATIONS AND DIPOLE MOMENT OF 1,4-DICHLORO-2-BUTYNE

$P_E + P_A = 1.05\ MR_D$ (assumed) = 29.8 cc.

| Temperature °K | No. of observations | Pressure range mmHg | Polarization cc. | Mean deviation of polarization | Dipole moment $D$. |
|---|---|---|---|---|---|
| 364.8 | 9 | 34- 56 | 102.9 | 0.9 cc. | $2.09_1$ |
| 372.3 | 14 | 32- 73 | 100.5 | 2.1 | $2.07_9$ |
| 392.3 | 10 | 43- 92 | 97.9 | 0.9 | $2.09_3$ |
| 414.1 | 10 | 45- 81 | 93.7 | 1.0 | $2.08_2$ |
| 433.3 | 9 | 51-161 | 90.8 | 1.2 | $2.08_1$ |

previous results in solutions. If we assume the hindering potential of the form of $V=(V_0/2)(1-\cos\theta)$, $V_0$ is found to be less than 0.1 kcal./mole. This result confirms the results of the electron diffraction investigation on this molecule recently made by Morino and Kuchitsu⁵⁾ that in the gaseous state this molecule has no preferred position for the internal rotation.

It should be noted that the component of the $CH_2Cl$ group moment perpendicular to the C—C≡C—C axis is found to be 1.47 $D$. If we assume the C—C—Cl angle of 111°⁵⁾, this corresponds to the C-Cl moment of 1.57 $D$, which is appreciably smaller than the normal C—Cl moment, 1.86 $D$. Pauling, Gordy and Saylor⁶⁾ suggested that propargyl chloride $CH\equiv C-CH_2Cl$ resonates between the two formulas $CH\equiv C-CH_2Cl$ and $C^+H=C=CH_2\ Cl^-$, and this resonance brings about the elongation of the C—Cl bond and the contraction of the adjacent C—C bond. If the resonance of this type takes place also in dichlorobutyne, it would produce an increase of the dipole moment of the $CH_2Cl$ group, but not its decrease. Therefore, the observed decrease of the said group moment denies Pauling's resonance scheme, or at least, it indicates that the predominant form is not Pauling's one.

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5) Y. Morino and K. Kuchitsu, This Bulletin, (to be published).

6) L. Pauling, W. Gordy and J. H. Saylor, *J. Am. Chem. Soc.* **64**, 1753 (1942).