An Electron Diffraction Investigation of the Molecular Structure of 1,4-Dichlorobutyne. II. A Study of Internal Rotation by Use of Halos in Small Angle Region*

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1. Introduction

The internal rotation of two methyl groups in dimethylacetylene has been investigated by several authors. The measurements of heat capacity[1,2], and the third-law entropy[3] offered a proof of practically complete absence of hindrance to the rotation of these methyl groups (less than 500 cal./mole)[2]. The analysis of the rotational structure of the perpendicular-type infrared bands[4,5] led to the conclusion that the assumption of unrestricted internal rotation is consistent with their observed data, thus giving independent support to the results of the thermal measurements.

As for the substituted dimethylacetylene[6], the complex microwave spectrum[7] of $CH_3—C\equiv C—CF_3$ was explained satisfactorily on the basis of a zero, or very low potential barrier when centrifugal distortion effects were taken into account[8], and $ClCH_2—C\equiv C—CH_2Cl$ molecule was shown, by means of temperature dependence of the dipole moment in the vapor state[9], to have a barrier of less than 0.1 kcal./mole, while in carbon tetrachloride and benzene solutions[10] the barrier was estimated to

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1) B. L. Crawford, Jr. and W. W. Rice, *J. Chem. Phys.*, **7**, 437 (1939).

2) G. B. Kistiakowsky and W. W. Rice, ibid., **8**, 618 (1940).

3) D. W. Osborne, C. S. Garner and D. M. Yost, ibid., **8**, 131 (1940).

4) D. R. J. Boyd, H. W. Thompson and R. L. Williams, *Disc. Faraday Soc.*, **9**, 154 (1950).

5) J. M. Mills and H. W. Thompson, *Proc. Roy. Soc.*, **A226**, 306 (1954).

6) A recent investigation of the vibrational spectrum of CF_3-C$\equiv$C-CF_3 by Miller and Bauman (*J. Chem. Phys.*, **22**, 1544 (1954)) has shown that this molecule follows D_{3d} selection rules, so that it is in either staggered configuration or free rotation. (R. P. Bauman, *J. Chem. Phys.*, **24**, 13 (1956)). However, no definite decision has yet been given.

7) B. Bak, L. Hansen and J. Rastrup-Andersen, *J. Chem. Phys.*, **21**, 1612 (1953).

8) D. R. Lide and D. Kivelson, ibid., **23**, 2191 (1955).

9) Y. Morino, I. Miyagawa, T. Chiba and T. Shimozawa, This Bulletin, **30**, 222 (1957).

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

be 0.75±0.20 kcal./mole. It is the main purpose of this article to apply the sector-microphotometer method of electron diffraction to the study of the internal rotation of 1,4-dichloro-2-butyne, using the structural data obtained in the preceding article[11], and to confirm the results of dipole moment measurement. This method will provide one of the effective means of determining the potential barrier of such a molecule, because a heavy chlorine atom is included in each of the rotating groups so that the diffraction pattern will show essential dependence on the internal rotation of these groups.

2. Experimental and Results

In order to study the internal rotation of this molecule, it is necessary to examine small-angle halos ($q \lesssim 15$). The theoretical intensity curves remain almost unchanged in this range when slightly different frame parameters (distances, angles, and mean amplitudes) are assumed, so that the essential features of the curves are determined by the assumption of the potential barrier alone. In the outer q region, on the other hand, the contribution from the Cl—Cl and H—Cl distances which change with the internal rotation damps rapidly, and in addition even a slight change of the frame parameters might cause a significant effect to the intensity curve enough to obscure the difference caused by the change of the potential barrier. Thus the photographs taken at the long camera length of about 27.9cm. ($q=5\sim27$) can be used as a means of estimating the potential barrier. The detail of the experimental procedure and numerical computation are given in the preceding article[11]. However, the usual technique of drawing the background line cannot be applied in this region. Karle's criterion of the non-negative Gaussian RD peaks[12a] is not applicable because the influence of f-factors upon the molecular intensity curve is not negligible in this region; nor can the background line be drawn through the zero-points of a reasonable theoretical curve[12b,13,14], because there is no zero-point from $q=5$ to 15. Consequently, we have to use some alternative standard for obtaining a reasonable background line. In this study a procedure similar to, but somewhat different from that of Bregman and Bauer[14] was used.

Assuming various types of potential barrier $V(\phi)$, theoretical intensity curves $M_c(q, V)$ were calculated from Eqs. (2) and (4) of Paper (I)[15]; the frame parameters were fixed at the values obtained in Paper (I), since the influence of their uncertainty was found to be negligible. To each M_c-curve the corresponding "background function" $I_b(q, V)$ was computed by the following formula:

$$I_b(q, V)=q^{1/2}I_o(q)/\{1+0.84M_c(q, V)\} \qquad (1)$$

where $I_o(q)$ is the observed total scattering intensity, which was multiplied by $q^{1/2}$ to accentuate the oscillations in the region $q=8\sim15$. The absolute molecular intensity M_c was multiplied[16] by 0.84 to make it fit the experimental curve in the region $q=16.7$ to 20.0.

If the diffraction experiment were ideally performed and the assumed model were strictly correct, the I_b-function should have no sudden fluctuation of the frequency of the order of molecular intensity[17]; in general, the corresponding I_b-function will approach to a smooth curve as the assumed model becomes better. Thus the extent of its fluctuation from a smooth curve can be used as a criterion for choosing reasonable models, provided that the corrections for a non-ideal experiment are properly taken into account.

For simplicity, only the first term of the potential function

$$V(\phi)=\frac{1}{2}V_1(1-\cos\phi)+\frac{1}{2}V_2(1-\cos 2\phi)+\frac{1}{2}V_3(1-\cos 3\phi)+\cdots\cdots, \qquad (2)$$

is considered first; the variable ϕ is the angle of rotation from the *trans* position. When free internal rotation ($V_1=0$) is assumed, the corresponding I_b-curve contains little fluctuation (Fig. 1A), which shows that this model is satisfactory. When the rigid *trans* structure ($V_1=\infty$) is assumed, the corresponding I_b-curve has much greater fluctuations, indicating that this model is definitely unacceptable (Fig. 2A). In a similar fashion, the I_b-curve based on the assumption that $V_1=1$ kcal./mole is also unsatisfactory because it still has some fluctuations (Fig. 3A). This implies that, so far as the cosine-type barrier is assumed, free internal rotation is the

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[11] K. Kuchitsu, This Bulletin, **30**, 391 (1957) (hereafter referred to as paper (I)).

[12a] J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957, 963 (1950).

[12b] I. L. Karle and J. Karle, ibid., **17**, 1052 (1949).

[13] J. M. Hastings and S. H. Bauer, ibid., **18**, 13 (1950).

[14] J. Bregman and S. H. Bauer, *J. Am. Chem. Soc.*, **77**, 1955 (1955).

[15] The following formula was used:

$$qM_c(q, V)=\{\sum_{\varphi}\sum_{i>j}(c_{ij}/r_{ij})\exp(-b_{ij}q^2)\times\sin(\pi q r_{ij}(\phi)/10)\exp(-V(\phi)/RT)\varDelta\phi\}/\{\sum_{\phi}\exp(-V(\phi)/RT)\}\ ,$$

where $\varDelta\phi$ is 10° and b_{ij} is a constant.

[16] The ratio of the observed molecular intensity to the theoretical one is always less than unity, since the background is raised by multiple and extraneous scattering. Even if the factor 0.84 is changed slightly, the conclusion given below is not altered essentially.

[17] An ideal background line (atomic and inelastic scattering) is known to be a smooth function of q. Multiple scattering will also cause an essentially smooth background (Ref. (12a)); and extraneous scattering was found, by measuring a photograph taken without sample, to have no sudden change in intensity. Other possible sources of sudden change, such as grain irregularities, small particles of dusts on the plate, accidental error in the photometry procedure, etc., may be eliminated by rotating the plate while scanning, and by averaging among sets of plates. The smoothness of the background line is discussed more extensively in the authors' recent study on n-propyl chloride, (Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, to be published). See also Ref. (11) of Karle's paper (Ref. (12b)).

most favorable model, V_1 being apparently less than 1 kcal./mole, although further quantitative estimation of its upper limit is difficult.

An alternative examination of the potential barrier is a comparison of the molecular intensity curve $qM_o(q)$, which is obtained by drawing a smooth background in such a way as to reproduce the theoretical intensity curve qM_c as closely as possible, in the resulting qM_o-curve. The model $V_1=\infty$ is completely unsatisfactory because these curves disagree with each other (Fig. 2B); the qM_c-curve for the model $V_1=1$ kcal./mole shows features near $q=8$ and 12.5 which cannot be reproduced in the qM_o-curve (Fig. 3B). However, the qM_c-curve based on the model $V_1=0$ is reproduced satisfactorily by the corresponding qM_o-curve. (Fig. 1B). A factor σ defined by the following equation may be used as a numerical measure of the overall inconsistency between the qM_c- and qM_o-curves:

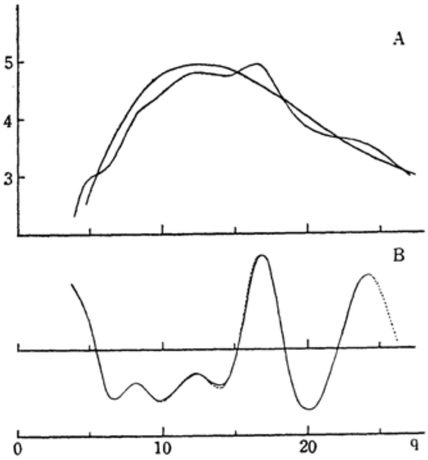

Fig. 1. (A) The observed intensity curve multiplied by $q^{1/2}$ obtained from the long camera-length photographs, and the I_b-curve for free internal rotation. (B) The qM_o-curve (solid line) which was obtained by drawing a smooth background line in such a way as to reproduce the theoretical intensity curve qM_c (dotted line) for free internal rotation as closely as possible.

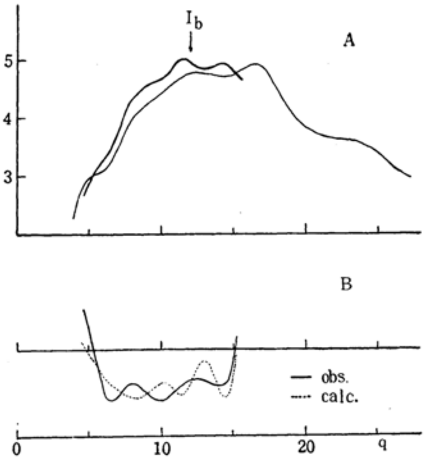

Fig. 2. (A) The I_b-curve for the rigid-*trans* model; the curve shows fluctuations with the frequencies of the order of molecular intensity. (B) The qM_c-curve (solid line) and the qM_c-curve (dotted line) for the rigid-*trans* model.

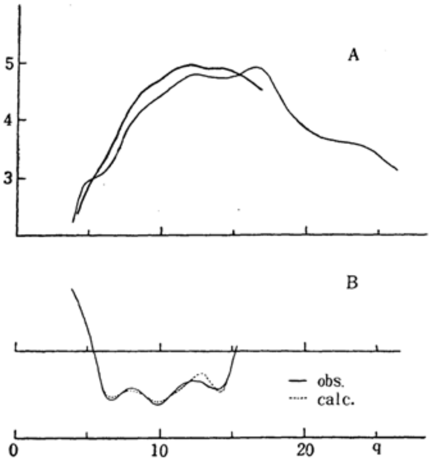

Fig. 3. (A) The I_b-curve for the model $V_1=1$ kcal./mole. (B) The qM_o-curve (solid line) and the qM_c-curve (dotted line) for the model $V_1=1$ kcal./mole.

$$\sigma=\sum_q\{qM_o(q)-cqM_c(q)\}^2, \qquad (3)$$

where the summation is taken over the integral q values from 5 to 14, and c is a numerical factor adjusted to minimize the σ-value. Table I shows that the lower the barrier, the less σ-value may be obtained, which again favors practically free internal rotation.

TABLE I

THE σ FACTORS OF THE THEORETICAL CURVES CALCULATED BY ASSUMING VARIOUS TYPES OF POTENTIAL BARRIERS

Assumption	$V=0$	$V=1$ kcal.	$V=\infty$
V_1 term only	0.0070	0.0173	0.2165
V_2 term only	0.0070	0.0261	0.1016
V_3 term only	0.0070	0.0082	0.0163

The σ value among the two observed curves is about 0.0002.

Similar procedure can be applied for a potential function of any shape. If, for example, the potential function is assumed to have only the second term (the *trans* and the *cis* positions being the lowest ones), a high potential barrier is found to be impossible, and the σ-factor has the lowest value when V_2 is zero; so too is this the case when only the third term (the *trans* and the *gauche* positions being the stable ones) is assumed, although the fact is less prominent than in the above cases (Table I). The actual potential barrier will naturally be neither of these extreme cases but a certain combination of these terms; nevertheless, it can be inferred from the above result that the internal rotation is practically unrestricted; in other words, the barrier higher than 1 kcal./mole is improbable.

3. Discussion

It is to be noted, in the first place, that the electron diffraction study, particularly the analysis of small angle halos, provides one method of investigating internal rotation. By the measurement of dipole moment, only the V_1-term can be determined[18]; on the contrary, more than one coefficient of the potential function (2) can be estimated, at least in principle, by the electron diffraction method if sufficiently accurate scattering data are available, although its precise evaluation is limited because of the difficulty in drawing a correct background line and in estimating experimental errors.

The analysis of 1,4-dichloro-2-butyne described above indicates that free internal rotation is in good agreement with the electron diffraction data, whereas a high potential barrier is inconsistent. This conclusion is consistent with that obtained from the dipole moment measurement of this molecule in the gaseous state; Morino and his collaborators[9] observed finite and constant values of the dipole moment, 2.08–2.09 D, in the temperature range of 90–160°C., from which they concluded that the V_1-coefficient of the potential function (2) is less than 0.1 kcal./mole.

It is well known that the potential barriers in ethane derivatives, such as 1,2-dichloroethane, are several kcal./mole[19]. The barrier in 1,4-dichloro-2-butyne is therefore much lower. This difference in barrier height arises mainly from the fact that the distance of the two rotating groups is longer in the latter molecule. In fact, the steric repulsion between the two C—Cl bond moments is shown to be only about 0.5 kcal./mole by a simple calculation[10].

Summary

The internal rotation of 1,4-dichloro-2-butyne was investigated by the sector-microphotometer method of electron diffraction, examining the region of smaller scattering angles ($q \lesssim 15$); photographs taken at a long camera length were analyzed using a criterion that the "background function" should have no sudden fluctuation. Free internal rotation is in good agreement with the observed scattering data, and a high potential barrier is inconsistent.

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[18] I. Miyagawa, *J. Chem. Soc. Japan*, **75**, 970 (1954).

[19] S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press Inc., New York (1954).