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AN INVESTIGATION OF THE STRUCTURE OF BUTADIENE BY HIGH RESOLUTION INFRA-RED AND RAMAN SPECTROSCOPY

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Abstract—The rotational Raman spectra of butadiene and butadiene-d_6 are found to consist of discrete lines having small (≈ 0.4 cm^{-1}) yet almost constant spacings, as would be expected for symmetric or nearly symmetric top molecules. An infra-red absorption band (Type C) of butadiene at 908 cm^{-1} is observed to have a spacing of about 2.5 cm^{-1}. Both the Raman and infra-red spectra provide evidence for the *trans* structure of the butadiene molecule. From the rotational constants A'' and $\bar{B}''$ the following structural parameters were obtained: $\angle(C{=}C{-}C) = 122.9 \pm 0.5°$ and $r(C{-}C) = 1.47_4 \pm 0.010$ Å (somewhat shorter than recently determined from electron-diffraction experiments).

A INTRODUCTION

THE butadiene molecule has proven to be a very useful example in discussions of valence theory, particularly in the calculation of fractional bond orders and the prediction of bond lengths. Yet, because of experimental difficulties and because of the rather complex structure of the butadiene molecule there have been only a few attempts to determine experimentally its structural parameters.[1] The most complete structural determination published so far is that of Almenningen, Bastiansen and Traetteberg who used the electron-diffraction technique. According to them the molecule has the *planar trans* configuration with $r(C{=}C) = 1.337 \pm 0.005$ Å, $r(C{-}C) = 1.483 \pm 0.01$ Å, $r(C{-}H) = 1.082 \pm 0.01$ Å, $\angle C{=}C{-}C = 122.4°$ and $\angle C{=}C{-}H = 119.8°$.

The purpose of the present paper is to report on the results of a high resolution study of the infra-red and Raman spectra of butadiene and on the information about the molecular structure obtained from these spectra.

B THE INFRA-RED ABSORPTION BAND OF BUTADIENE AT 908 cm^{-1}

Most hydrocarbons containing a vinyl group have a strong infra-red absorption band near 900 cm^{-1} which is due to the hydrogen out-of-plane wagging motion of the C=CH$_2$ group.[2] An analysis of the vibration-rotation structure of this band in butadiene was undertaken in order to provide information about the rotational constants of the molecule, and in particular to confirm that it has the *trans* configuration.

The infra-red spectrum was measured on a grating spectrometer described previously[3] which had been modified to improve the uniformity of the grating drive.

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[1] V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.* 61, 1769 (1939); A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* 12, 1221 (1958).

[2] N. Sheppard and D. M. Simpson, *Quart. Rev.* 6, 1 (1952).

[3] R. N. Dixon, *Spectrochim. Acta* 9, 59 (1957).

A Merton-type replica grating of 2500 lines per inch was used close to the first-order blaze at 10 μ. The detector was a Hilger-Schwarz thermocouple used with optical and D.C. amplification.

The absorption band is illustrated in Fig. 1. It is a Type C band, that is a perpendicular band in the limiting case of a symmetric top. Only the K structure was resolved and the measured line positions are listed in Table 1. The combination differences ${}^RQ_K - {}^PQ_K$ and sums ${}^RQ_K + {}^PQ_K$ were plotted respectively against K and K^2 (Fig. 2) and from these the following band constants were obtained

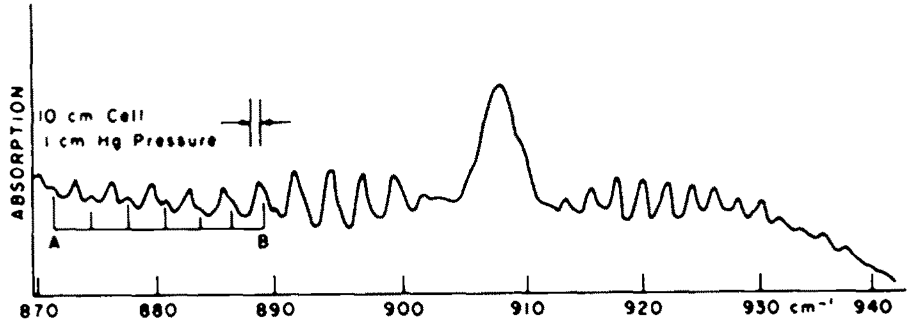

FIG. 1. The infrared absorption band of 1,3 butadiene centered near 908 cm^{-1}
(Slit width = 0·8 cm^{-1})

TABLE 1. Absorption maxima for the CH$_2$ "wagging mode" of 1,3-butadiene

K	${}^RQ_K$ (cm^{-1})	${}^PQ_K$ (cm^{-1})	${}^RQ_K - {}^PQ_K$ (cm^{-1})	${}^RQ_K + {}^PQ_K$ (cm^{-1})
0	-			-
1				
2	913·60			
3	915·65	901·80	13·85	1817·45
4	917·70	899·38	18·32	1817·08
5	919·80	896·80	23·00	1816·60
6	921·90	894·00	27·90	1815·90
7	923·93	891·18	32·75	1815·11
8	925·90	888·25	37·65	1814·15
9	927·80	885·40	42·40	1813·20
10	929·70	882·50	47·20	1812·20
11	931·60	879·50	52·10	1811·10
12	933·30	876·40	56·90	1809·70
13	935·00	873·30	61·70	1808·30
14	936·80	870·13	66·67	1806·93
15	938·35	-	-	-

$$(A' - \bar{B}') - (A'' - \bar{B}'') = 0{\cdot}0287 \pm 0{\cdot}0008 \text{ cm}^{-1}$$

$$(A' - \bar{B}') = 1{\cdot}20 \pm 0{\cdot}01 \text{ cm}^{-1}$$

$$(A'' - \bar{B}'') = 1{\cdot}229 \pm 0{\cdot}01 \text{ cm}^{-1}$$

$$\nu_0 + (A' - \bar{B}') = 908{\cdot}96 \text{ cm}^{-1}$$

The Q 'lines' can thus be represented by the formula $\nu = 908{\cdot}96 \pm 2{\cdot}40\,K - 0{\cdot}029\,K^2$, and the band origin ν_0 is at 907·76 cm^{-1}. A second set of lines, shown in Fig. 1 between A and B, has the same spacing as the main series and is probably caused by a 'hot' band.

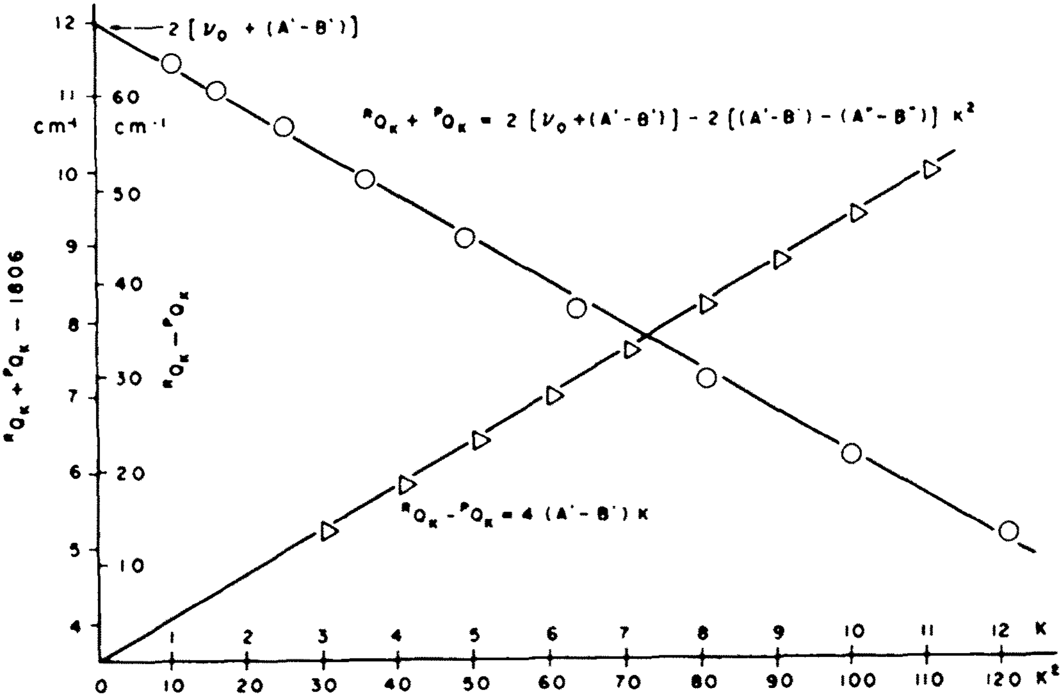

FIG. 2. Graphs of the relations $^RQ_K - {}^PQ_K$ vs K and $^RQ_K + {}^PQ_K$ vs K^2 for the 908 cm^{-1} band.

C. THE ROTATIONAL RAMAN SPECTRUM OF BUTADIENE

The pure rotational Raman spectrum of butadiene vapour at 15 cm Hg pressure was excited by the Hg 4358 line and photographed with a 21 ft grating spectrograph.[4] A rather simple line spectrum was observed as shown in Fig. 3. A similar spectrum, but with a narrower line spacing, was observed with butadiene-d$_6$. These spectra resemble the rotational spectra of symmetric or nearly symmetric tops. For nearly symmetric top molecules K remains a good quantum number and the selection rules for rotational transitions of symmetric tops in the Raman effect (namely $\Delta K = 0$, $\Delta J = 1, 2$) still hold approximately. In the butadiene spectra only the S branch lines ($\Delta K = 0$; $\Delta J = 2$) were observed. Their frequencies are listed in Table 2.

The analyses of the spectra were carried out in the usual way making use of the symmetric top equation for the frequencies of the S lines

$$\Delta\nu = 4B''(J + 3/2) - 8D_J''(J + 3/2)^3$$

but with B'' replaced by $\bar{B}'' = \frac{1}{2}(B'' + C'')$. Graphs of $\Delta\nu/(J + 3/2)$ vs. $(J + 3/2)^2$

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[4] B. P. Stoicheff, *Advances in Spectroscopy* (Edited by H. W. Thompson) Vol 1, p 91 Interscience, New York (1959). *Canad. J. Phys.* 32, 330 (1954).

TABLE 2. Frequency shifts of the rotational Raman lines of butadiene and 1,3-butadiene-d_6

J	$(\Delta\nu)$ cm^{-1} $H_2C=CH-CH=CH_2$	 $D_2C=CD-CD=CD_2$
17	10·470	
18	11·033	
19	11·595	
20	12·188	
21	12·718	
22	13·283	
23	13·826	
24	14·422	
25	14·989	
26	15·536	
27	16·111	13·179
28	16·658	13·653
29	17·206	14·105
30	17·776	14·548
31	18·304	15·008
32	18·803	15·468
33	19·433	15·929
34	19·997	16·404
35	20·569	16·840
36	21·187	17·306
37	21·737	17·775
38	22·320	18·256
39	22·882	18·726
40	23·444	—
41	24·009	19·671
42	24·563	20·125
43	25·130	20·539
44	25·690	20·993
45	26·256	21·470
46	26·819	21·932
47	27·368	22·375
48	27·935	22·824
49	28·488	23·293
50	28·914	23·732
51	29·590	—
52	30·188	—
53	30·774	25·235
54	31·338	25·686
55	31·929	26·142
56	32·485	26·578
57	33·060	27·009
58	33·639	27·456
59	34·182	27·910
60	34·730	
61	35·283	
62	35·849	

gave the values $\tilde{B}'' = 0{\cdot}1413 \pm 0{\cdot}0002\ \mathrm{cm}^{-1}$ and $0{\cdot}1155 \pm 0{\cdot}0002\ \mathrm{cm}^{-1}$ for C_4H_6 and C_4D_6 respectively (and $D_J'' \approx 1 \times 10^{-8}\ \mathrm{cm}^{-1}$ for both). When combined with the value of $(A'' - \tilde{B}'')$ obtained from the infra-red band, this $\tilde{B}''$ value leads to $A'' = 1{\cdot}370 \pm 0{\cdot}011\ \mathrm{cm}^{-1}$.

D. THE STRUCTURE OF BUTADIENE

The present spectroscopic results confirm the *trans* configuration of the butadiene molecule. A discrete rotational Raman spectrum would only be expected for the *trans* form since it deviates only slightly from a symmetric top whereas the *cis* form has a much larger deviation. For the latter, one would expect a complicated spectrum which would probably not be resolved under the conditions of the present experiment. The correctness of the above argument is supported by the rotational spectra of the *trans* and *cis* butene-2 molecules[4] included in Fig. 3: only the spectrum of the *trans* form has a discrete structure. Moreover, for butadiene the observed spacing of about $2{\cdot}5\ \mathrm{cm}^{-1}$ in the infra-red band can be explained only by the *trans* form: for the *cis* form a spacing of about $1{\cdot}0\ \mathrm{cm}^{-1}$ would be expected. Indeed the value of $A'' - \tilde{B}'' = 1{\cdot}229\ \mathrm{cm}^{-1}$ observed here agrees quite well with that calculated from the structural parameters of butadiene given by Almenningen *et al.*[1], namely $A'' - \tilde{B}'' = 1{\cdot}213\ \mathrm{cm}^{-1}$.

The spectroscopic results are not sufficient to determine the complete structure of the molecule, nor do they alone give definite proof for the planarity of butadiene. Nevertheless, if values of the CH_2 and CH parameters are assumed, it is possible to obtain reasonably accurate values of the parameters of the C=C—C=C group from the spectroscopic data. This method was adopted in the present calculations.

The following assumptions were made:

(1) butadiene is planar, that is, $I_C = I_B + I_A$

(2) all CH bonds have $r = 1{\cdot}085$ Å

(3) $\angle HCH = 120°$, $\angle CCH = 120°$.

It was then possible to calculate values of $r(C—C)$ and I_A as functions of $\angle(C=C—C)$ for various values of $r(C=C)$ from the observed value of $\tilde{B}''$. These results are shown in graphical form in Figs. 4 and 5. (The observed value of $\tilde{B}''$ for butadiene-d_6 confirms these results but unfortunately does not lead to additional information.) The observed value of $I_A = (20{\cdot}43 \pm 0{\cdot}17) \times 10^{-40}\ \mathrm{g\ cm}^2$ then leads to the relation (Fig. 5).

$$\angle(C=C—C) \pm 0{\cdot}5° = 149{\cdot}65 - 20\, r(C=C)$$

The relation between $r(C—C)$ and $\angle(C=C—C)$ shown in Fig. 4 expressed in equation form is

$$r(C—C) = 5{\cdot}716 - 1{\cdot}70\, r(C=C) - 0{\cdot}016\, \angle(C=C—C);$$

When the above relation for $\angle(C=C—C)$ is substituted it reduces to

$$r(C—C) \pm 0{\cdot}008\ \text{Å} = 3{\cdot}3216 - 1{\cdot}380\, r(C=C)$$

This relation is represented by the broken lines in Fig. 4.

According to Almenningen *et al.*[1], the most accurately determined parameter of butadiene is the C=C bond length, $r(C=C) = 1{\cdot}337 \pm 0{\cdot}005$ Å. It is in good

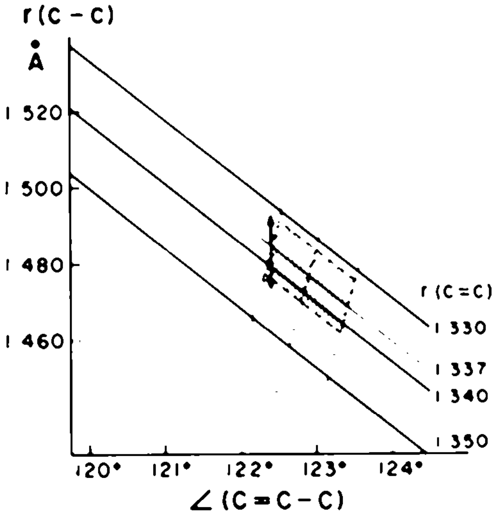

FIG. 4. Graph of r(C—C) vs. ∠(C=C—C) for various values of r(C=C) consistent with the observed value of $\tilde{B}''$. The hatched area represents the values of r(C—C) consistent with the observed value of I_A and r(C=C) = 1·337 ± 0·005 Å. The vertical arrow represents the value of r(C—C) determined by electron-diffraction experiments.

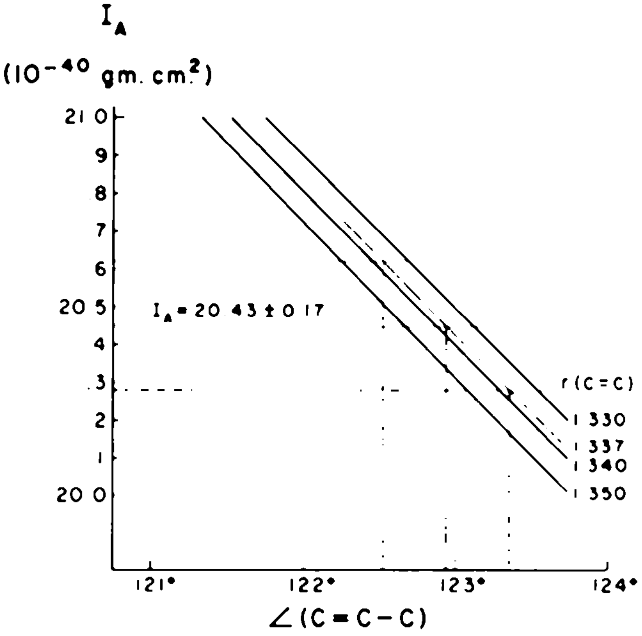

FIG. 5. Graph of I_A vs. ∠(C=C—C) for various values of r(C=C) consistent with the observed value of $\tilde{B}''$.

agreement with recent values of the C=C bond length in ethylene, namely 1·334 Å[5], 1·337 Å[6] and 1·339 Å[7]. If this value of r(C=C) = 1·337 Å is now taken over, the spectroscopic results give the related values of r(C—C) and ∠(C=C—C) represented by the hatched area of Fig. 4:

$$r(\mathrm{C{-}C}) = 1{\cdot}476 \pm 0{\cdot}010\ \text{Å}$$
$$\angle(\mathrm{C{=}C{-}C}) = 122{\cdot}9 \pm 0{\cdot}5^{\circ}$$

For purposes of comparison the values obtained by electron diffraction are indicated by the vertical arrowhead in Fig. 4. It may be mentioned that the electron-diffraction analysis indicates an unsymmetrical error distribution for r(C—C), making an error of + 0·01 Å less probable than an error of − 0·01 Å.

In conclusion, the spectroscopic data are in agreement with the structural parameters determined by electron diffraction within the quoted limits, although the spectroscopic data slightly favour a C—C bond length shorter by about 0·01 Å and a C=C—C angle larger by about 0·5° than the electron-diffraction values. Even so, this shorter value for the C—C bond length in butadiene still gives an appreciably higher value than would be expected (~1.460 Å) from the observed linear relation of the variation of C—C bond lengths with the total number of atoms adjacent to the C—C bond.[8]

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