pression of about 5° when mixed with the hydrocarbon $C_{38}H_{42}$, m. p. 133°, obtained by action of sodium amalgam and water on the dimer. It is probably identical with this last compound.

**Reduction of the Dimer with Hydrogen Iodide.**—A solution of 0.6 g. of the dimer in 40 cc. of glacial acetic acid was refluxed with 2 g. of red phosphorus and 10 cc. of 47% hydrogen iodide solution for ten hours. From this reaction mixture a product, m. p. 134–135°, was obtained. It showed only a slight depression in melting point when mixed with the product obtained by reducing the dimer with sodium and amyl alcohol.

*Anal.* Calcd. for $C_{38}H_{42}$: C, 91.56; H, 8.44; mol. wt., 498. Found: C, 91.33; H, 8.49; mol. wt. (Rast), 435.

**Oxidation of the Dimer.**—A solution of 1 g. of the dimer in 20 cc. of glacial acetic acid was refluxed for eight hours with 3 g. of potassium dichromate. No acidic substances were isolated from the oxidation mixture. A small amount of a neutral product, m. p. 227°, after crystallization from ether was isolated.

*Anal.* Calcd. for $C_{26}H_{26}O_2$: C, 84.3; H, 7.02. Found: C, 84.29; H, 7.05.

No benzophenone could be detected in the products of oxidation.

## Summary

The structure of the hydrocarbon $C_{38}H_{38}$, which forms when tetraphenyldi-*t*-butylethynylethane undergoes rearrangement, has been found to be that of a diallene, 1,1,6,6-tetraphenyl-4,5-di-*t*-butyl-1,2,4,5-hexatetraene. Many reactions of this and closely related compounds have been investigated.

URBANA, ILLINOIS RECEIVED OCTOBER 11, 1935

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[PUBLICATION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 514]

# The Spectrum and the Force Constants of the Ethylene Molecule

BY LYMAN G. BONNER

## Introduction

The first investigation of the infra-red absorption spectrum of ethylene gas was made by Coblentz[1] in 1905. Using a prism spectrometer he was able to locate a number of absorption maxima but did not resolve any of the fine structure. In 1928, Levin and Meyer[2] reinvestigated the spectrum of this molecule, using higher dispersion instruments and taking greater care to obtain pure gas and to exclude atmospheric effects. In the region 2–15 μ they found a total of ten absorption bands, most of which were at least indicated on Coblentz' prism curve.

The spectrum of ethylene in the photographic region of the infra-red has been investigated by Badger and Binder,[3] who found only one band, at 8720 Å.

The most recent work on the Raman spectrum of this molecule was carried out by Dickinson, Dillon and Rassetti.[4] They used the gas at high pressure and mercury resonance excitation and found a total of six lines.

Any attempt to obtain a complete vibrational analysis of ethylene, for force constant evaluation, showed, however, that there were a good many gaps and inconsistencies in the experimental data. There has been made, then, in the present work, a complete reinvestigation of the photographic, infra-red, and Raman spectra. The results of this work lead to a satisfactory determination of eleven of the twelve fundamental vibration frequencies of the ethylene molecule, and permit an estimate to be made of the twelfth.

Eleven new absorption bands have been found in the photographic infra-red. Experiments using liquid ethylene have shown the presence of three new Raman lines, and have failed to show two of those reported by Dickinson, Dillon and Rassetti.

## Experimental

All infra-red absorption experiments were done with the stainless steel absorption tube and twenty-one foot grating spectrograph recently constructed in this Laboratory.[4a] The tube measures approximately seven-eighths inch in diameter and it has a maximum length of seventy feet. The full length was used in investigations of all regions of the spectrum except that beyond 10,000 Å. For this region, due to the low sensitivity of all available plates, it was necessary to reduce the path length to twenty-eight feet. Pressures of gas used in the tube ranged from one to seven atmospheres and the entire spectral region investigated lay between 6000 and 12,000 Å. Eastman spectroscopic plates were used for wave lengths below 10,300 Å., but for longer wave lengths their sensitivity was too low, even with the reduced tube length.

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(1) W. W. Coblentz, *Carnegie Inst. Wash. Publ.*, 35 (1905).

(2) A. Levin and C. F. Meyer, *J. Opt. Soc. Am.* and *Rev. Sci. Instr.*, **16**, 137 (1928).

(3) R. M. Badger and J. L. Binder, *Phys. Rev.*, **38**, 1442 (1931).

(4) Dickinson, Dillon and Rassetti, *ibid.*, **34**, 582 (1929).

(4a) R. M. Badger, L. G. Bonner and P. C. Cross, *J. Opt. Soc. Am.*, **25**, 355 (1935).

The Eastman plates were always hypersensitized before using by treating for one minute with a 4% ammonia solution at 10°. One series of measurements was made in the region 10,000–12,000 Å. using special Agfa infra-red plates very kindly supplied by Dr. T. J. Dunham, Jr., of the Mt. Wilson Observatory.

The ethylene used in these experiments was a commercial product, supplied for anesthetic purposes, and guaranteed by the manufacturers to be better than 99% pure.

Raman scattering experiments were made on gaseous ethylene using λ 2537 excitation, but under these conditions only the three strong lines reported by Dickinson, Dillon and Rassetti[4] were found. Experiments were then made with the liquid in the hope of obtaining a larger number of shifts. Two types of experiment were made, one using glass apparatus and λ 4358 excitation, and the other with quartz and λ 2537. In each case liquid ethylene was confined in a tube about 15 mm. in diameter and 20 cm. long. This was then immersed in a Dewar flask filled with a mixture of alcohol and solid carbon dioxide. At this temperature, −72°, the vapor pressure of ethylene is about 4.8 atmospheres. The Dewar was silvered on one side only, and the light from a mercury arc lamp was passed through the clear side. The scattered light was then focused by means of a prism and lens on the slit of a prism spectrograph. For the glass apparatus, the dispersion of the spectrograph was about 50 Å. per mm., and for the quartz, 10 Å. per mm. In the case of the excitation with visible light, the use of a filter seemed advisable, in order to restrict as far as possible the number of exciting lines and to reduce the continuous background from the arc. For this purpose an aqueous solution of quinine and cobalt sulfate in a 15-mm. cell placed between lamp and Dewar served quite well. This filter effectively removed all the lines but that at 4358 Å.

A total of seven Raman lines was observed. Three quite strong ones were measured with frequency shifts of 3009, 1619 and 1341 cm.$^{-1}$. Dickinson, Dillon and Rassetti[4] measured these same lines in the gas at 3019.3, 1623.3, and 1342.4 cm.$^{-1}$ so it may be seen that, for the low frequency lines particularly, the shift in passing from the gas to the liquid is not large. However, gas values will be used wherever possible. In addition to the three strong lines there were four weak ones measured at 3069, 2880, 1654 and 950 cm.$^{-1}$. The last one in particular was extremely weak and diffuse, and in consequence the measurement may be in error by as much as 10 cm.$^{-1}$. The line at 2880 cm.$^{-1}$ was observed by the previous investigators and was given by them as somewhat weaker than a pair, also observed, at 3240 and 3272 cm.$^{-1}$. Since in these experiments the line at 2880 showed up quite definitely but no trace was obtained of the other two they may probably be regarded as spurious.

## Assignment of Frequencies

In Fig. 1 are shown diagrams of the twelve fundamental modes of vibration of ethylene as given by R. Mecke.[5] The first pair of letters following each mode gives its symmetry to rotations of $\pi$ about the axes of greatest and least moment of inertia, respectively. Thus mode 4 is antisymmetrical to a rotation of 180° about the axis of greatest moment of inertia (the axis perpendicular to the plane of the figure), but symmetrical to the same rotation about the axis of least moment of inertia (the figure axis). Of the letters in brackets, R indicates that the fundamental is active in the Raman spectrum, I that it is active in the infra-red, and In that it is completely inactive. Since the molecule possesses a center of symmetry, no modes may be active in both Raman and infra-red spectra. Linear combinations must be made of the bracketed modes to obtain the true vibration forms.

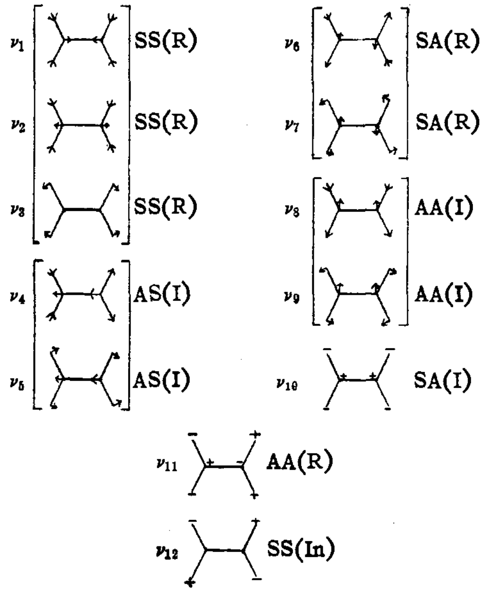

Fig. 1.—The fundamental modes of vibration of ethylene.

From the figure it may be seen that, on the basis of symmetry, there are three types of fundamental active in the infra-red, and each of these is typified by its distinctive band envelope. The type AS is recognized by its sharp central maximum, or Q branch. The type AA has no central maximum and appears, under low resolution, as a widely spaced doublet. The type SA can have no real Q branch, but may appear to have a small one due to piling up of lines near the center of the band. These two last types are distinguished, under low resolution, by a series of widely spaced maxima.

The three modes $\nu_1$, $\nu_2$, $\nu_3$ are of the completely symmetrical type, and should appear very strongly in the Raman effect, so to these may be assigned at once the three strong observed Raman lines.

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(5) R. Mecke, *Z. physik. Chem.*, **B17**, 1 (1932).

The assignment of frequencies to the remainder of the modes is not at all such a clear-cut case. Table I shows what seems at present to be the most reasonable assignment of frequencies to the fundamental modes and to the combinations and overtones appearing in the infra-red and Raman spectra.

In assigning the infra-red frequencies the following principles have been used. First, if two or more modes are excited simultaneously the symmetry of the combination level is the product of the symmetries of the individual modes. The multiplication of symmetries obeys the same law as the multiplication of signs: S × S = S, A × A = S, S × A = A. The type of the band resulting from a transition from the ground state to this combination level is that associated with the symmetry of the level. Thus, if a mode of symmetry AA combines with one of symmetry SA the resultant level is of symmetry AS and the band resulting from a combination of this with the ground level is of the Q branch type. It follows from this that any combination leading to the symmetry SS cannot appear in the infra-red. The second principle is that no two inactive fundamentals can combine to give an infra-red active band. The justification for this last is that it seems improbable that two vibrations, neither of which alone produces a change in electric moment, should combine in such a way as to produce this change.

In Table I the columns headed $V_1$, $V_2$, etc., give the quantum numbers of the upper level. The lower level is in all cases the ground level. The column headed "Type" tells whether the band possesses a Q branch (Q) or has a doublet structure (D). The last column gives the calculated frequencies of the combination bands. The large discrepancies, for the higher combinations, between observed and calculated frequencies are not

TABLE I

ASSIGNMENT OF TRANSITION FREQUENCIES

| Frequency (cm.$^{-1}$) Infra-red | Type | $V_1$ | $V_2$ | $V_3$ | $V_4$ | $V_5$ | $V_6$ | $V_7$ | $V_8$ | $V_9$ | $V_{10}$ | $V_{11}$ | $V_{12}$ | Calculated frequency |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 950 | D | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | ... |
| 940 | D | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | ... |
| 1443.9 | Q | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | ... |
| 1724 | ? | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | ... |
| 1889.7 | Q | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 1890 |
| 2047.0 | Q | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 2040 |
| 2988.2 | Q | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | ... |
| 3107.4 | D | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | ... |
| 4207.9 | D | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 4192 |
| 4324.3 | D | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 4294 |
| 4515.5 | D | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 4513 |
| 4729.0 | D | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 4730 |
| 8757.5[a] | Q | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8965 |
| 8981.0[a] | Q | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 9203 |
| 9138.6[a] | D | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 9322 |
| 9775.7[a] | Q | 0 | 0 | 0 | 2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 9995 |
| 9814.5[a] | Q | 0 | 0 | 0 | 2 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 10034 |
| 10119[a] | D | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 2 | 0 | 0 | 1 | 0 | 10303 |
| 10293.2[a] | Q | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 10545 |
| 10363.4[a] | Q | 1 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10588 |
| 11465 | D | 1 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 11538 |
| 11724[a] | Q | 0 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 11984 |
| 11780[a] | D | 0 | 0 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 12034 |
| 14100[a] | ? | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 14941 |
| Raman | | | | | | | | | | | | | | |
| 950[a] | | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | ... |
| 1342.4 | | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | ... |
| 1623.3 | | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | ... |
| 1654[a] | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | ... |
| 2880.1 | | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 2850 |
| 3019.3 | | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | ... |
| 3069[a] | | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | ... |

[a] Reported for the first time in this paper,

unreasonable when one considers that the convergence factors for a hydrogen-containing molecule are of necessity rather large.

The infra-red band at 949.7 cm.$^{-1}$ is almost without a doubt not a single band but a superposition of two fundamentals. In fact, from the absorption curve published by Levin and Meyer the maxima belonging to each may be picked out, and from this the spacing seems to be about 10 cm.$^{-1}$. It is interesting that three fundamentals seem to fall in the region of 950 cm.$^{-1}$, and this fact leads to some ambiguity in the assignments. It is in some cases impossible to tell whether a given band is an harmonic containing $\nu_7$, $\nu_9$ or $\nu_{10}$. The frequency $\nu_{11}$ has not yet appeared in the spectrum although it should be active in the Raman effect. However, the infra-red band at 2047 cm.$^{-1}$ is almost without a doubt a combination of this with one of the 950 cm.$^{-1}$ frequencies, thus fixing $\nu_{11}$ at about 1100 cm.$^{-1}$. $\nu_{12}$ cannot appear alone in either the infra-red or Raman spectrum, but Eucken and Parts,[6] from specific heat data, have estimated it to lie in the region 750–800 cm.$^{-1}$. If the weak absorption reported by Coblentz[1] at 1724 cm.$^{-1}$ is real, it could be a combination of $\nu_{12}$ with one of the 950 cm.$^{-1}$ fundamentals, thereby locating $\nu_{12}$ at about 775 cm.$^{-1}$, in good agreement with Eucken and Parts.[6] Other possibilities are, however, that the weak Raman line observed in the present work at 1654 cm.$^{-1}$ is either the first overtone of this frequency, which would be permitted, or a combination of it with a 950 cm.$^{-1}$ band. This would give to $\nu_{12}$ the values 825 or 700 cm.$^{-1}$. Considering the nature of the specific heat estimation either one of these would be in about as good agreement with experiment as the above value of 775 cm.$^{-1}$. It is at present impossible to make a unique choice and to state definitely the value of the $\nu_{12}$ fundamental. However, the Raman line is certainly real, and there is considerable doubt as to the infra-red band. Also the overtone would, in this case, be more likely to appear than the combination, thus giving some weight to the 825 cm.$^{-1}$ value.

TABLE II

| Vibration | Frequency | Vibration | Frequency |
|---|---|---|---|
| $\nu_1$ | 1623.3 | $\nu_7$ | 950 |
| $\nu_2$ | 3019.3 | $\nu_8$ | 3107.4 |
| $\nu_3$ | 1342.4 | $\nu_9$ | 950 |
| $\nu_4$ | 2988.2 | $\nu_{10}$ | 940 |
| $\nu_5$ | 1443.9 | $\nu_{11}$ | 1100 |
| $\nu_6$ | 3069 | $\nu_{12}$ | 825 |

In concluding this section, it might be desirable to give a table showing the frequencies at present assigned to all the fundamental vibrational modes of the ethylene molecule.

### Evaluation of the Force Constants

The most important results to be obtained from such an evaluation of the fundamental vibration frequencies of a molecule as has been made in the previous section, are the values of the force constants of the bonds holding the atoms together. These force constants together with such constants for the interaction forces between bonds as may be obtained are of interest for the deeper insight they give into the nature of intramolecular forces. For a really accurate evaluation of bond force constants the mechanical frequencies for infinitesimal amplitudes of vibration should be used, but for most molecules, particularly the more complicated ones, the data are insufficient to obtain these, so the observed frequencies must be used. It is probable, though, that for most types of vibration the deviations will not be so large as to affect the calculated force constants greatly.

The expressions relating the fundamental frequencies with the bond force constants and other constants of the ethylene molecule have been derived by Dr. E. B. Wilson, Jr. I wish at this point to thank Dr. Wilson for his kindness in permitting me to use these formulas before their publication.

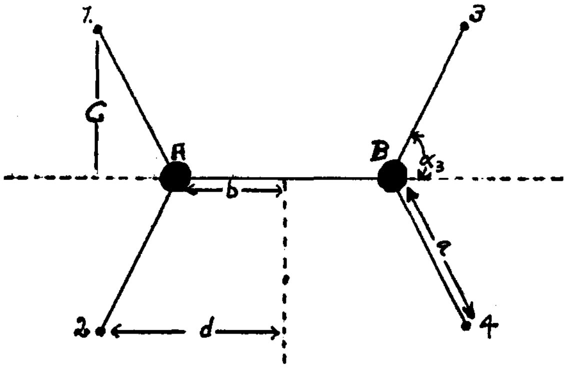

Fig. 2.—Assumed structure of the ethylene molecule: ●, is carbon; •, is hydrogen.

Figure 2 shows the assumed structure of the ethylene molecule.

A somewhat simplified potential function containing eight constants may now be written down as follows

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(6) Eucken and Parts, *Z. physik. Chem.*, **B20**, 184 (1933).

$$\begin{aligned}2V = K(\Delta R)^2 + q\Sigma(\Delta S_{\mathrm{i}})^2 + Ha^2\Sigma(\Delta\alpha_{\mathrm{i}})^2 + \\ ha^2\Sigma\mu_{\mathrm{i}}^2 + 2L\{\Delta S_1\Delta S_2 + \Delta S_3\Delta S_4\} + \\ 2\theta a^2\{\Delta\alpha_1\Delta\alpha_2 + \Delta\alpha_3\Delta\alpha_4\} + 2\Lambda a^2\{\Delta\alpha_1\Delta\alpha_3 + \\ \Delta\alpha_2\Delta\alpha_4\} + 2\Omega a^2\{\mu_1\mu_3 + \mu_2\mu_4\}\end{aligned}$$

Here $\Delta R$ refers to stretch of the C–C bond, $\Delta S_{\mathrm{i}}$ to stretch of the C–H$_{\mathrm{i}}$ bond, $\Delta\alpha_{\mathrm{i}}$ to bending of the C–H$_{\mathrm{i}}$ bond in the plane and $\mu_{\mathrm{i}}$ to bending of the C–H$_{\mathrm{i}}$ out of the plane.

The secular determinant in terms of the constants and of the frequency parameter, $\lambda$, factors into sub-determinants corresponding to the bracketed modes of Fig. 1. These factors may now be written down for each of the sets of modes.

The following abbreviations have been adopted.

$m$ = mass of hydrogen $\quad M$ = mass of carbon

$\beta = \cos\alpha \quad \gamma = \sin\alpha$

$$N = 1 + 2\frac{m}{M}\gamma^2 \qquad E = 2\frac{m}{M}\frac{a + b\beta}{b}\gamma$$

$$F = 1 + 2\frac{m}{M}\left(\frac{a + b\beta}{b}\right)^2 \qquad P = 2\frac{m}{M}\beta\gamma$$

$$Q = 1 + 2\frac{m}{M}\beta^2$$

The frequency expressions are as follows.

$\nu_1, \nu_2, \nu_3$

$$\begin{vmatrix} K + \beta^2(q + L) + \gamma^2(H + \theta + \Lambda) - {}^1/{}_2M\lambda & -\beta(q + L) & (H + \theta + \Lambda)\gamma \\ -\beta(q + L) & (q + L) - m\lambda & 0 \\ (H + \theta + \Lambda)\gamma & 0 & (H + \theta + \Lambda) - m\lambda \end{vmatrix} = 0$$

$\nu_4, \nu_5$

$$\lambda = \frac{1}{2m}\left\{Qq' + NH' \pm [(Qq' + NH')^2 - 4q'H'(NQ - P^2)]^{1/2}\right\}$$

$$q' = q + L \qquad H' = H + \theta - \Lambda$$

$\nu_6, \nu_7$

$$\lambda = \frac{1}{2m}\left\{Nq'' + FH'' \pm [(Nq'' + FH'')^2 - 4q''H''(NF - E^2)]^{1/2}\right\}$$

$$q'' = q - L \qquad H'' = H - \theta - \Lambda$$

$\nu_8, \nu_9$

$$\lambda = \frac{1}{2m}\left\{Nq'' + QH''' \pm [(Nq'' + QH''')^2 - 4q''H'''(NQ - P^2)]^{1/2}\right\}$$

$$q'' = q - L \qquad H''' = H - \theta + \Lambda$$

$\nu_{10}$

$$\lambda = (h + \Omega)\frac{2m + M}{mM}$$

$\nu_{11}$

$$\lambda = (h - \Omega)\frac{2md^2 + Mb^2}{mMb^2}$$

If we assume the dimensions of the ethylene molecule obtained by Badger[7] to be correct, *viz.*: C—H = 1.04 Å., C=C = 1.37 Å. and $\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{H}}$ angle = 126°, we are in a position to compute values for these constants. It is to be noted that the five constants $q$, $L$, $H$, $\theta$ and $\Lambda$ occur in all the expressions for the first nine frequencies so there will be ample opportunity for checks on their values.

Due to approximations in choosing the potential function the cubic factor for $\nu_1$, $\nu_2$, $\nu_3$ has no real solution for the force constants. However, by a variation method it has been possible to find the values of the force constants which give frequency values fitting most closely to the observed values. These are probably quite close to the true values. In Table III are given the values of the force constants or force constant combinations occurring in the expressions for each frequency set.

TABLE III

| | | |
|---|---|---|
| $\nu_1, \nu_2, \nu_3$ | $K = 8.2 \times 10^5$ dynes/cm. | $H + \theta + \Lambda = 1.18 \times 10^5$ dynes/cm. |
| | $q + L = 5.09$ | |
| $\nu_4, \nu_5$ | $q + L = 5.08$ | $H + \theta - \Lambda = 1.09$ |
| $\nu_6, \nu_7$ | $q - L = 4.88$ | $H - \theta - \Lambda = 0.34$ |
| $\nu_8, \nu_9$ | $q - L = 5.02$ | $H - \theta + \Lambda = 0.52$ |
| $\nu_{10}$ | $h + \Omega = 0.45$ | |
| $\nu_{11}$ | $h - \Omega = 0.37$ | |

It can be seen that the values of $q + L$ and of $q - L$ calculated from two different frequency sets check satisfactorily. Also, if the values of $H$, $\theta$ and $\Lambda$ be determined from the second, third and fourth sets, the value of $H + \theta + \Lambda$ so obtained is 1.26 × 10$^5$ as compared with 1.18 obtained above, which is satisfactory when the nature of the solution obtained for the cubic factor is considered.

It is now possible to give a table of the values of all the individual force constants used in this work.

TABLE IV

| | |
|---|---|
| $K = 8.2 \times 10^5$ dynes/cm. | $\theta = 0.38 \times 10^5$ dynes/cm. |
| $q = 5.02$ | $\Lambda = 0.09$ |
| $L = 0.07$ | $h = 0.41$ |
| $H = 0.80$ | $\Omega = 0.04$ |

The interaction constants are all quite small except for the constant $\theta$. The size of this, comparable with the primary constant $H$, is a result of the definition in the potential function. The half angle in the CH$_2$ bond was used as the coördinate, and hence interactions between the two half angles of the same bond appear quite large. A different choice of coördinates, one in which the entire angle was used, would lead to a much smaller value of the apparent interaction.

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(7) R. M. Badger, *Phys. Rev.*, **45**, 648 (1934).

### Abstract

In the present study of the ethylene molecule there has been made a complete reinvestigation of the Raman spectrum and of the infra-red absorption spectrum in the photographic region. Three new Raman lines have been found and eleven new infra-red absorption bands. Using these new data it has been possible to assign reasonable frequency values to all the twelve fundamental vibration modes of the ethylene molecule. From these frequency values, and the necessary formulas, eight of the force constants of the molecule have been obtained.

PASADENA, CALIF. RECEIVED OCTOBER 14, 1935

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# Ring Closure Studies in the Sugar Benzoates

BY M. L. WOLFROM AND CLARENCE C. CHRISTMAN

The work herein reported is a continuation of the ring closure studies in acylated sugar derivatives previously reported from this Laboratory.[1] The general procedure used in these studies is to treat a sugar mercaptal with trityl (triphenylmethyl) chloride. The extensive investigations of Helferich and co-workers[2] have shown that this reagent reacts preferentially with primary alcohol groups and the resultant ether is readily split with halogen acids to regenerate the original hydroxyl group. The tritylated mercaptal is then acylated. On removal of the trityl group and hydrolysis of the mercapto groups with mercuric chloride and moist acetone in the presence of cadmium carbonate,[3] ring closure on the open hydroxyl group may be effected. It was hoped that this ring closure would be on the terminal hydroxyl group, thus producing a $<1,6>$ ring in the hexose series and the normal or $<1,5>$ ring in the pentose series. Definite evidence that the trityl group had entered the terminal position was available for the glucose benzoate and galactose acetate series.

The work of Micheel and co-workers,[4] first performed through reactions not involving tritylation, has shown that a $<1,6>$ or septanose structure is obtained in the galactose acetate series on further acetylation of the resultant tetraacetate. We found it necessary to leave the acetate series and enter the benzoate series in order to obtain crystalline derivatives. With glucose, the series of reactions described above resulted in the formation of the normal or pyranose ring as the end-product and a benzoyl shift had thus occurred. The tetrabenzoate obtained was identical with the ordinary form of glucose tetrabenzoate, which is generally assigned to the pyranose series, although in the case of this particular substance, this assignment cannot be considered as absolutely proved.

In the work herein reported the series of reactions described above has been extended to the galactose benzoate series. In the glucose benzoate compounds,[1] detritylation was always accompanied by halogenation of the terminal hydroxyl group and subsequent hydrolytic reactions were required to remove this halogen atom. With the galactose benzoates, conditions for detritylation unaccompanied by halogenation could be found although by changing these conditions, halogenation could be likewise readily effected. The final compound was a galactose tetrabenzoate which crystallized with one mole of methanol and like the corresponding acetate was probably an *aldehydo*-form. Due to the lack of known isomers in the sugar benzoate series, this structure could not be definitely determined. Further benzoylation of this tetrabenzoate did not produce a crystalline product, although benzoylation of $\alpha$-galactose yielded a readily crystallizable $\alpha$-galactose pentabenzoate.

Application of the same series of reactions to *d*-mannose diethyl mercaptal produced a crystalline diethyl mercaptal tetrabenzoate. Removal of the mercapto groups yielded a mannose tetrabenzoate obtained in the form of a colorless powder that was analytically pure. Provided no benzoate shift had occurred, this substance may be

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(1) M. L. Wolfrom, J. L. Quinn and C. C. Christman, THIS JOURNAL, **56**, 2789 (1934); *ibid.*, **57**, 713 (1935).

(2) B. Helferich and J. Becker, *Ann.*, **440**, 1 (1924); B. Helferich, *Z. angew. Chem.*, **41**, 871 (1928).

(3) M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

(4) F. Micheel and F. Suckfüll, *Ann.*, **502**, 85 (1933); *ibid.*, **507**, 138 (1933); *Ber.*, **66**, 1957 (1933); F. Micheel and W. Spruck, *ibid.*, **67**, 1665 (1934).