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Microwave Spectra of Thiophene, 2- and 3-Monodeutero, 3,3'-Dideutero, and Tetradeuterothiophene. Structure of the Thiophene Molecule

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2- and 3-monodeutero, 3,3'-dideutero, and tetradeuterothiophene have been prepared and their microwave spectra recorded together with the microwave spectrum of ordinary thiophene (C_4H_4S). Lines originating from the 4% content of $C_4H_4S^{34}$ and the 2% content of $C_3C^{13}H_4S$ in ordinary thiophene (both the 2- and the 3- C^{13} species) were also identified. For all isotopic species rotational constants of high accuracy were obtained. The total material is sufficient for a complete determination of all the 8 geometrical parameters of thiophene.

I. INTRODUCTION

THE present microwave investigation of thiophene and some of its deuterated derivatives was undertaken as a natural continuation of previous papers on pyridine,¹ furan,² and pyrrole.³ Microwave absorption of ordinary thiophene has been searched for by C. H. Townes and E. B. Wilson⁴ but no lines were found in the 18 000–26 000 MHz region investigated. We are unable to explain this since the thiophene lines found by us are of approximate intensity 10^{-7} – 10^{-8} cm⁻¹. The dipole moment of thiophene (~ 0.6 D) is close to the dipole moment of furan (~ 0.7 D), also investigated by us.² The asymmetry parameter, κ , is however about zero for thiophene while it is close to unity for furan. Thus, the thiophene microwave spectrum does not exhibit the accumulation of Q -branch lines which is found for nearly symmetrical tops like furan.

II. EXPERIMENTAL PART

A. Preparation of Materials

Since the preparation of pure, partially deuterated species of thiophene has never been described we shall account for our procedure briefly.

2-Deuterothiophene was prepared from 8 g magnesium and 34 g (0.16 mole) 2-iodothiophene (bp 73.0–73.5°C at 15 mm pressure),⁴ dissolved in 100 cc anhydrous ether. The Grignard-compound was formed very easily in the course of 75 minutes after which it was decomposed by means of 13 g D_2O . After reflux for 90 minutes, the reaction mixture was cooled to 0°C and filtered. The ether solution was dried over $CaCl_2$, filtered from the drying agent, and carefully fractionated. 8.0 g deuterated thiophene (0.094 mole), boiling at 83.5–83.7°C (762 mm) was collected (yield 59%). The infrared absorption curve of the sample, taken on a Beckmann IR 2 instrument, unequivocally showed that it was not a mixture of

deuterated species. A trace of ordinary thiophene (about 3%) could be seen. Since no mixture of deuterated species was obtained one may be sure that the sample is 2-deuterothiophene. The microwave investigation confirmed this conclusion.

3-Deuterothiophene. It had originally been hoped that this and other deuterated thiophenes could be prepared by using the Grignard technique as above. Since we were unable to initiate a reaction between 3-iodothiophene and magnesium, the following alternate standard procedure had to be adopted. At room temperature 10 g (0.048 mole) 3-iodothiophene (bp 82.5–83.0°C at 15 mm)⁴ was added to the mixture of D_2O and CH_3COOD (0.14 mole acid), resulting from the reaction between 25 g D_2O and 7 g $(CH_3CO)_2O$. 16 g of carefully dried Zn-dust was introduced and the whole mixture was refluxed for 75 minutes under exclusion of atmospheric moisture, the flask being immersed in a bath of boiling water. After cooling, thiophene, some water, and, perhaps, a little CH_3COOD was distilled off *in vacuo* under temperature and pressure control so that the distillation could be interrupted when practically all thiophene had been collected. Most of the water in the distillate was removed mechanically with a syringe. The remaining moist thiophene was dried, first over anhydrous Na_2CO_3 which also removes CH_3COOD , then over P_2O_5 . Finally it was distilled into a weighed ampule. Both drying and distillation was carried out in an evacuated system. The yield was 2.70 g deuterated thiophene (0.032 mole; yield 66%). By the same criteria as above it could be concluded that the sample was 3-deuterothiophene, contaminated with a small amount of ordinary thiophene (about 3%) but e.g. with no trace of the 2-deutero derivative.

3,3'-Dideuterothiophene was prepared quite analogously from 12 g (0.036 mole) 3,3'-di-iodothiophene (bp 153.5–153.7° at 15 mm)⁴ and the same quantities of D_2O , CH_3COOD , and Zn-dust as above. The reduction took 75 minutes at 100°C and the deuterated thiophene was isolated as described above. The yield was 2.00 g (64%). Except for a trace of ordinary thiophene it was pure 3,3'-dideuterothiophene.

Tetradeuterothiophene. 20 g (0.034 mole) tetraiodothiophene (mp 203°C) was treated with 16 g Zn-dust

* U. S. National Science Foundation, post-doctoral fellow.

¹ Bak, Hansen, and Rastrup-Andersen, J. Chem. Phys. 22, 2013 (1954).

² Bak, Hansen, and Rastrup-Andersen, Discussions Faraday Soc. 19, 30 (1955).

³ Bak, Christensen, Hansen, and Rastrup-Andersen, J. Chem. Phys. 24, 720 (1956).

⁴ Private communication to H. D. Hartough, *Thiophene and Its Derivatives* (Interscience Publishers Inc., New York, 1952).

TABLE I. Observed and calculated microwave absorption frequencies (in MHz) of thiophene and four deuterated thiophenes in the 17 500–29 100 MHz region.

Transition	Thiophene			2-deuterothiophene			3-deuterothiophene			3,3'-dideuterothiophene			Tetradeuterothiophene		
	Obs	Calc	Diff	Obs	Calc	Diff	Obs	Calc	Diff	Obs	Calc	Diff	Obs	Calc	Diff
1 ₁₀ →2 ₁₁	19 490.2	19 490.1	0.1	19 372.4	19 372.7	−0.3	18 519.8	18 519.7	0.1	17 729.6	17 729.5	0.1	17 527.9	17 527.9	0
2 ₂₁ →3 ₂₂	25 961.8	25 961.7	0.1	25 636.3	25 636.3	0	24 730.6	24 730.1	0.5	23 701.5	23 701.5	0	23 149.6	23 149.6	0
2 ₂₀ →3 ₂₁	28 879.1	28 879.2	−0.1	29 044.7	29 044.5	0.2	27 325.5	27 325.3	0.2	26 110.8	26 110.5	0.3	26 373.5	26 373.6	−0.1
2 ₁₁ →3 ₁₂	28 488.6	28 488.5	0.1	28 056.1	28 056.4	−0.3	27 144.7	27 144.6	0.1	26 016.3	26 016.2	0.1	25 297.2	25 297.2	0
2 ₁₂ →3 ₁₃	22 202.3	22 202.2	0.1	21 617.0	21 617.6	−0.6	21 254.5	21 255.0	−0.5	20 415.8	20 416.0	−0.2	19 433.8	19 433.9	−0.1
2 ₀₂ →3 ₀₃	23 043.8	23 044.2	−0.4	22 227.9	22 228.1	0.2	22 134.5	22 135.0	−0.5	21 292.2	21 292.4	−0.2	19 925.3	19 925.7	−0.4
4 ₁₃ →4 ₁₄							19 012.5	19 012.5	0	18 109.1	18 109.4	−0.3			
6 ₂₄ →6 ₂₅	24 377.0	24 377.0	0	25 528.1	25 528.0	0.1	22 549.0	22 549.0	0	21 299.7	21 299.8	−0.1	23 332.0	23 332.1	−0.1
7 ₃₄ →7 ₃₅	19 089.0	19 088.2	0.8	22 034.3	22 034.0	0.3							20 651.9	20 651.9	0
8 ₃₅ →8 ₃₆							25 470.2	25 470.3	−0.1	23 827.0	23 827.6	−0.6			
9 ₄₆ →9 ₄₇	21 547.5	21 546.9	0.6	26 289.8	26 290.1	−0.3	18 569.8	18 569.3	0.5				24 899.3	24 899.4	−0.1
10 ₅₆ →10 ₅₇				20 514.0	20 513.2	0.8	27 851.2	27 852.0	−0.8	25 769.8	25 770.3	−0.5	20 293.9	20 294.0	−0.1
11 ₅₆ →11 ₅₇	23 652.9	23 652.8	0.1				19 749.1	19 749.5	−0.4	17 731.0	17 730.2	0.8			
12 ₅₇ →12 ₅₈										27 185.0	27 185.2	−0.2			
12 ₆₆ →12 ₆₇				23 976.1	23 976.8	−0.7							24 048.8	24 050.0	−1.2

and the reaction products from 25 g D₂O and 14 g (CH₃CO)₂O (0.28 mole acid) under reflux in a flask immersed in an oil bath kept at 120–130°C for a period of 20 hours. The appearance of deuterated thiophene in the reflux condenser began considerably later than in the foregoing cases. 1.10 g deuterated thiophene was isolated in the usual way (yield 37%). Both infrared and microwave spectra confirmed that almost pure tetra-deuterothiophene had been collected.

Simple Zn-dust reduction of halogenated aromatic compounds in acidified D₂O thus has proved to be very successful for the preparation of partially deuterated species, both here and in some of our earlier work.¹ It is noteworthy that the reduction takes place whether the reactants are miscible¹ or not (this paper). In neither case does undesired exchange occur. Also, the examples studied by us have involved both chloro-, bromo-, and iodo-compounds.

B. Measurement of Microwave Absorption Frequencies and Identification of the Lines

The microwave spectrograph used was of the conventional Stark-modulated type with a local frequency standard tested against spectral lines of well-known frequency. The experimental square-wave peak voltage applied was 400–800 volts/cm. In some cases the square-wave had to be biased by a dc voltage ranging from 1000–2000 volts/cm in order to resolve the Stark components. All measured frequencies (Table I) are thought to be accurate to ± 0.1 MHz. All *R*-branch lines could be unambiguously identified by their Stark-pattern. This made a pretty accurate prediction of the position of the *Q*-branch lines possible after which the actual position of the *Q*-lines was ordinarily easily determined since the spectra with which we are concerned here are not very rich in lines. Of course, all *Q*-line assignments were tested by means of the usual $\nu_{\text{obs}}/\Delta E(\kappa)$ versus κ plot.

Prior to the search for lines originating from the 4% content of C₄H₄S³⁴ present in ordinary thiophene, we prepared a mixture of 4% tetradeuterothiophene and 96% ordinary thiophene. With vapors of this mixture

in the spectrograph we found optimum conditions for the observation of the 1₁₀→2₁₁ transition at 17 527.9 MHz and the 2₂₁→3₂₂ transition at 23 149.6 MHz in tetra-deuterothiophene. The Stark-pattern of both lines could be seen. The intensity was about 3 to 5 times the noise level of the spectrograph, the 2₂₁→3₂₂ line being somewhat stronger than the 1₁₀→2₁₁ line. Under the assumption that the two C, H distances in thiophene are both equal to 1.075 Å, consistent with earlier microwave work^{1–3} and electron-diffraction investigations⁵ on related substances, a tentative model of thiophene was calculated (compare next paragraph) from the measured principal moments of inertia given in Table II. Based on this model a precalculation of the position of the 1₁₀→2₁₁ and the 2₂₁→3₂₂ transitions in C₄H₄S³⁴ was carried out. Lines of suitable intensity and Stark-pattern were found experimentally, close to the calculated positions. The measured absorption frequencies are given in Table III. These data, of course, permitted us to improve the thiophene model. Based on this refined model the positions of the 2₂₁→3₂₂ transitions in C¹³(2)C₃H₄S and C¹³(3)C₃H₄S were precalculated. The observed transitions given in Table III and identified by their intensity and their Stark-pattern agreed to within 2–3 MHz (compare Sec. IV) with what was expected. The corresponding 1₁₀→2₁₁ transitions were too weak to be observed.

TABLE II. Rotational constants (*A, B, C*) in MHz, asymmetry parameter (κ) and principal moments of inertia (*I_a, I_b, I_c*) in a.m.u. Å² together with the quantum defect (Q.D.) for thiophene and four deuterated species.

	Thiophene	2-deuterothiophene	3-deuterothiophene	3,3'-dideuterothiophene	Tetradeuterothiophene
<i>A</i>	8041.77	7437.32	7856.13	7616.99	6587.67
<i>B</i>	5418.12	5413.61	5138.14	4914.50	4905.66
<i>C</i>	3235.77	3131.82	3105.23	2985.99	2810.88
κ	−0.09182	0.05994	−0.14420	−0.16713	0.10929
<i>I_a</i>	62.8568	67.9654	64.3422	66.3622	76.7313
<i>I_b</i>	93.2944	93.3721	98.3781	102.8549	103.0402
<i>I_c</i>	156.2164	161.4015	162.7836	169.2840	179.8299
Q.D.	0.0652	0.0640	0.0633	0.0669	0.0584

⁵ Almennigen, Bastiansen, and Hansen, *Acta Chem. Scand.* **9**, 1306 (1955).

TABLE III. Observed microwave absorption frequencies (in MHz) of $C_4H_4S^{34}$, $C^{13}(2)C_3H_4S$, and $C^{13}(3)C_3H_4S$.

	$C_4H_4S^{34}$	$C^{13}(2)C_3H_4S$	$C^{13}(3)C_3H_4S$
$1_{10} \rightarrow 2_{11}$	19 003.9
$2_{21} \rightarrow 3_{22}$	25 373.4	25 869.0	25 529.2

III. CALCULATION OF ROTATIONAL CONSTANTS

The rotational constants of the various isotopic molecules investigated with the exception of species containing S^{34} and C^{13} were calculated by first reading $(A-C)$ and κ from the Q -line plot. The values obtained were inserted in the expressions,

$$\begin{aligned}\nu(1_{10} \rightarrow 2_{11}) &= 2(A+C) + \frac{1}{2}(A-C)[3\kappa-1], \\ \nu(2_{21} \rightarrow 3_{22}) &= 3(A+C) + \frac{1}{2}(A-C)[3\kappa-3], \\ \nu(2_{20} \rightarrow 3_{21}) &= 3(A+C) + \frac{1}{2}(A-C)/ \\ &\quad [3\kappa-3+2(4\kappa^2+6\kappa+6)^{0.5}-2(\kappa^2+3)^{0.5}], \\ \nu(2_{11} \rightarrow 3_{12}) &= 3(A+C) + \frac{1}{2}(A-C)/ \\ &\quad [\kappa+3-2(4\kappa^2-6\kappa+6)^{0.5}], \\ \nu(2_{12} \rightarrow 3_{13}) &= 3(A+C) + \frac{1}{2}(A-C)/[\kappa+3-2(\kappa^2+15)^{0.5}], \\ \nu(2_{02} \rightarrow 3_{03}) &= 3(A+C) + \frac{1}{2}(A-C)/ \\ &\quad [3\kappa-3+2(\kappa^2+3)^{0.5}-2(4\kappa^2+6\kappa+6)^{0.5}],\end{aligned}$$

and 6 slightly different values of $(A+C)$ were calculated. The average of these 6 numbers we take as our measured $A+C$. With thiophene as a typical example ($A+C-11\,277$ MHz) were found to be 0.55, 0.51, 0.58, 0.57, 0.58, and 0.41. Therefore, $A+C$ was taken to $11\,277.54 \pm 0.05$ MHz. Since we had found $(A-C)/2 = 2403.0 \pm 0.2$ MHz from the Q -line plot, we conclude that $A = 8041.77 \pm 0.20$ MHz and $C = 3235.77 \pm 0.20$ MHz. κ (taken from the Q -line plot) is -0.09182 ± 0.00005 . From the definition of κ as a function of A , B , and C we then calculated $B = 5418.12 \pm 0.50$ MHz. Rotational constants for all isotopic species studied here, principal moments of inertia in a.m.u. A^2 , and the quantum defect (Q.D.) of all five species are collected in Table II. Microwave absorption frequencies calculated by means of these rotational constants are to be found in Table I.

For $C_4H_4S^{34}$ the A -value was taken equal to the A -value for C_4H_4S since A is the rotational constant referring to the two-fold axis of symmetry. Due to the quantum defect a small error is hereby committed but it has less influence on the final model of thiophene than the error in the frequency measurements. Since the frequencies of the two observed lines are simply $3B+3C$, $(2_{11} \rightarrow 3_{22})$ and $3B+C$, $(1_{10} \rightarrow 2_{11})$, B and C are

TABLE IV. Rotational constants (A, B, C) in MHz, asymmetry parameter (κ) and principal moments of inertia (I_a, I_b, I_c) in a.m.u. A^2 together with the quantum defect (Q.D.) for $C_4H_4S^{34}$.

A^a	B	C	κ	I_a	I_b	I_c	Q.D.
8041.77	5273.05	3184.75	-0.14009	62.8568	95.8611	158.7190	0.0011

^a Taken from thiophene.

easily obtained. Table IV contains the rotational constants etc. for $C_4H_4S^{34}$. No rotational constants were calculated for the $C^{13}C_3H_4S$ species.

IV. CALCULATION OF THE MOLECULAR STRUCTURE

Figure 1 shows how thiophene has been placed in a Cartesian coordinate system with its center of mass falling in the origin. Hydrogen coordinates are denoted by (a_i, b_i) where the subscript indicates the position. The coordinates of carbon and the sulfur atoms are correspondingly given by capital letters. As indicated in Fig. 1 thiophene is planar. This has already been concluded from infrared⁶ and Raman⁷ studies but a further proof may be obtained from Table II. Here, it is seen that I_c is very close to the sum of I_a and I_b , the quantum defect $(I_c - I_b - I_a)$ being very small and remarkably constant for five isotopic species.

Formulas quoted in our paper on pyridine¹ show how the coordinates of a specific atom in the coordinate

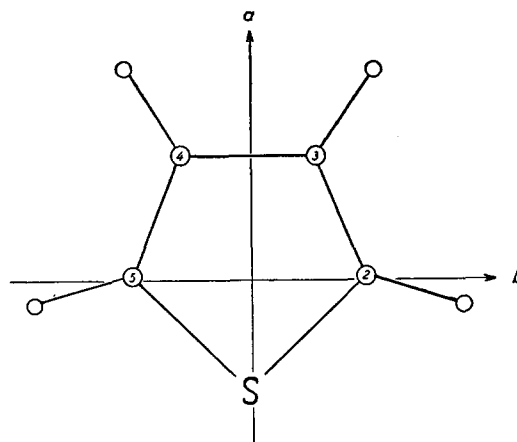


FIG. 1. Positions of thiophene atoms in relation to the principal axes of inertia (a, b, c) and the center of mass $(0,0,0)$ of the molecule. Valence angles and bond lengths have been drawn to scale.

system of Fig. 1 can be calculated from a knowledge of the principal moments of inertia of the "parent" molecule and the moments of the isotopic species in which the atom in question has been replaced by an isotope. Using these formulas we calculate the coordinates of the hydrogens and the sulfur atom from the material in Tables II and IV. Since any moment of inertia, I , of thiophene may be said to consist of contributions from the hydrogens (I^{4H}), the sulfur atom (I^S), and the four carbon atoms (I^{4C}) where $I = I^{4H} + I^S + I^{4C}$ we get that

$$m_C(2B_2^2 + 2B_3^2) = I_a - I_a^{4H}, \quad (1)$$

$$m_C(2A_2^2 + 2A_3^2) = I_b - I_b^{4H} - I_b^S, \quad (2)$$

$$m_SA_1 + m_C(2A_2 + 2A_3) = -m_H(2a_2 + 2a_3), \quad (3)$$

where Eq. (3) expresses that b is an axis through the

⁶ H. W. Thompson and R. B. Temple, Trans. Faraday Soc. **41**, 27 (1945).

⁷ A. W. Reitz, Z. physik. Chem. **B33**, 179 (1936); **B38**, 275 (1937).

center of mass. Equations (2) and (3) only contain the unknowns A_2 and A_3 . They were solved directly. Equation (1) combined with Eq. (4) to be given could be solved from our knowledge of one absorption line in each of the $C^{13}C_3H_4S$ spectra. Equation (4) expresses that the squares of the two C, H distances in thiophene deviate by the amount δ :

$$(B_2 - b_2)^2 + (A_2 - a_2)^2 - (A_3 - a_3)^2 - (B_3 - b_3)^2 = \delta. \quad (4)$$

The unknowns here are B_2 and B_3 . δ was now varied through the interval -0.030 to $+0.030$ Å². Solving Eqs. (1) and (4) for some of the values in this interval we could find B_2 and B_3 as functions of δ . Each set of B_2 , B_3 values corresponds to a definite thiophene model, since A_2 and A_3 had already been calculated. For thiophene $I_c = I_a + I_b + 0.0652$ a.m.u. Å². As the quantum defect was seen to be remarkably constant (Table II) we shall assume that

$$I_c' = I_a' + I_b' + 0.0652 \quad (5)$$

for both $C^{13}C_3H_4S$ species. The equations¹ connecting A_2 , B_2 with $I_a'(2)$, $I_b'(2)$ and A_3 , B_3 with $I_a'(3)$, $I_b'(3)$, respectively, were now solved with respect to the moments of inertia. By insertion in Eq. (5), $I_c'(2)$ and $I_c'(3)$ were calculated. Finally, the magnitude $3B + 3C$ which gives the location of the $2_{21} \rightarrow 3_{22}$ transition, could be calculated for both $C^{13}C_3H_4S$ species as a function of δ . The value of δ that gave agreement with the experimentally observed frequency 25 869.0 MHz in the $C^{13}(2)C_3H_4S$ -spectrum was found to be 0.033. Agreement for the other C^{13} -species was found for $\delta = 0.029$. The consistency between the two δ -values is satisfactory since the discrepancy is close to what must be expected due to the error in the frequency determination. If the assumption (5) is altered the agreement becomes less satisfactory. We may therefore take the consistency between the two δ -values as a verification of assumption (5). Values of the molecular parameters corresponding to $\delta = 0.031$ Å² were calculated. They are given in Table V where they may also be compared with the

TABLE V. Geometrical parameters of thiophene from the present microwave investigation, from electron-diffraction work,^a and from molecular orbital theory.^b Distances in Å.

Distances:	Microwaves	Electron-diffraction	Mol orbitals
C(2), H(2)	1.085	1.09 (assumed)	
C(3), H(3)	1.073	1.09 (assumed)	
C(2), S	1.718	1.74 ± 0.03	1.68
C(2), C(3)	1.352	1.35 (assumed)	1.38
C(3), C(4)	1.455	1.44 (assumed)	1.40
Angles:			
C(5)–S–C(2)	91°18'	91° ± 4°	
S–C(2)–C(3)	112°36'	112° ± 3°	
C(2)–C(3)–C(4)	111°45'	113° ± 3°	
S–C(2)–H(2)	119°06'	...	
C(4)–C(3)–H(3)	123°30'	...	

^a See reference 8.

^b See reference 9.

TABLE VI. Thiophene parameters from the microwave data of this paper *not* including the observed lines from the $C^{13}C_3H_4S$ species. Equality of the two C, H distances was assumed. Distances in Å.

Distances:		
C(2), H(2)	1.079	(1.085) ^a
C(3), H(3)	1.079	(1.073)
C(2), S	1.723	(1.718)
C(2), C(3)	1.360	(1.352)
C(3), C(4)	1.430	(1.455)
Angles:		
C(5)–S–C(2)	91°40'	(91°18')
S–C(2)–C(3)	111°37'	(112°36')
C(2)–C(3)–C(4)	112°33'	(111°45')
S–C(2)–H(2)	119°12'	(119°06')
C(4)–C(3)–H(3)	123°57'	(123°30')

^a Numbers in paranthesis are from the most probable model (column 2, Table V).

result of earlier electron-diffraction work,⁸ and a primitive molecular-orbital calculation by Longuet-Higgins.⁹

V. DISCUSSION

The thiophene model we have arrived at fits astonishingly well with the result obtained by electron-diffraction work. It deviates from the latter mainly in that *no* a priori assumptions had to be made. Also, the probable error in distances and angles is considerably diminished amounting to about 0.005 Å in the distances and about 30' in all angles. A rigorous treatment of the error problem, is, however, rather complicated since one cannot simply indicate uncertainty intervals for the parameters. Functional relationships between the deviations from the values of column 2, Table V would have to be given. In order to throw some light on the error problem we have calculated the thiophene parameters which result if one assumes that $\delta = 0$ (corresponding to equal C, H distances) and ignores the observation of the lines from the $C^{13}C_3H_4S$ species. Based on the parameters of column 2, Table VI the positions of the $2_{21} \rightarrow 3_{22}$ transitions in the $C^{13}C_3H_4S$ species are precalculated to be at 25 530.7 and 25 868.0 MHz. The experimental values are 25 529.2 and 25 869.0 MHz, respectively. The 1–2 MHz discrepancy is removed in the model of column 2, Table V.

In the literature, two alternative values of the length of a "normal" C=C distance can be found, 1.331 Å and 1.353 Å.^{10,11} Our measured C=C distance in the thiophene molecule of 1.352 Å is so close to the higher of these numbers that we believe that a lower value, maybe 1.331 Å, must be more correct. If a "normal" C=C distance is 1.353 Å it would mean that the supply of π -electrons which must be concentrated in the ab-

⁸ V. Schomaker and L. Pauling, J. Am. Chem. Soc. **61**, 1769 (1939).

⁹ H. C. Longuet-Higgins, Trans. Faraday Soc. **45**, 173 (1948).

¹⁰ H. W. Thompson, Trans. Faraday Soc. **35**, 697 (1939).

¹¹ W. S. Galloway and E. F. Barker, J. Chem. Phys. **10**, 88 (1942).

normally short C—C and C—S bonds in thiophene, had to be taken exclusively from the sulfur atom. As is easily seen this would result in a very high polarity of the molecule contradictory to its low dipole moment. If it is assumed, however, that the "normal" C=C distance lies close to 1.33 Å we find that about $0.40e$ have migrated from both C=C bonds in thiophene. $0.40e$ must be added to a normal C—C bond in order to produce the measured bond-length, 1.455 Å, of the short C—C bond in thiophene. Similarly, $0.50e$ must be added to each of the C—S bonds since a "normal" C—S bond is 1.818 Å.¹² $0.60e$ must, therefore, be taken from the sulfur atom. The π -electron moment resulting from these displacements of charge is about $0.6 \text{ D } \uparrow$ (directed from the positive sulfur towards the middle of the short C—C bond). Since the estimated σ -moment is of the order $1.5\text{--}2.0 \text{ D } \downarrow$, it means that the predicted resulting

¹² M. Shaw and J. J. Windle, *J. Chem. Phys.* **19**, 1063 (1951).

moment is $0.9\text{--}1.4 \text{ D } \downarrow$ as compared with the experimental value 0.6 D . The agreement is satisfactory, considering the approximate character of the way of estimating the dipole moment. Confirmation of the conclusion that the resulting dipole moment is directed towards the sulfur atom may be derived from the fact that 3-methyl thiophene has a *higher* dipole moment ($\sim 0.8 \text{ D}$) than thiophene.¹³

The experimental description of the thiophene molecule now seems so improved that a renewed theoretical treatment is justified. We intend to carry this out.

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¹³ R. Keswani and H. Freiser, *J. Am. Chem. Soc.* **71**, 1789 (1949).

Tunneling Through High Periodic Barriers. I*

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Analytic expressions for tunneling frequencies through high periodic barriers are derived. The expression for wells of threefold symmetry is applied to the analysis of microwave data on CH_3SiF_3 , CH_3SiH_3 , and CH_3SiD_3 and values of the barrier heights of 1 kcal, 1.5 kcal, and 1.5 kcal per mole, respectively, are obtained, which are in reasonable agreement with previously obtained values.

I. INTRODUCTION

THE phenomenon of tunneling through potential barriers, representing motions which are classically forbidden, is of importance in several branches of physics, among them the complexity of structure that such motions cause in microwave and infrared spectral lines and the drastic effects that they often have on the relaxation times and line widths of nuclear magnetic resonance spectra. The analysis of the phenomenon has two aspects *viz.*, the origin and nature of the potential barrier hindering the motion and secondly the solution of the relevant Schrödinger equation with the assumed form of the potential. Regarding the first one, there has as yet been no definite theory giving the form of the potentials, although some authors¹ have tried to explain them in a number of different cases. Happily, Dennison and Uhlenbeck,² in their analysis of the in-

version spectrum of ammonia corresponding to the inversion of the N of the NH_3 pyramid about the plane containing the H_3 triangle, have shown that the tunneling frequency is not critically dependent on the form assumed for the hindering potential. The form of the potential hindering the inversion in NH_3 consists of two adjacent minima separated by a hill and the walls going to infinity on either side. In the case of symmetric groups like CH_3 rotating internally relative to another symmetric group (or asymmetric as in the case of CH_3OH), the potential does not diverge anywhere but consists of a set of symmetrical equally spaced minima. It is of course more correct to take the potential function as a Fourier series

$$\sum_{\gamma} \frac{V_{\gamma}}{2} (1 + \cos N\gamma\phi),$$

ϕ being the angular coordinate defining the internal rotation of the rotating groups relative to each other. But for computational convenience, often only the term $\gamma=1$ is retained. As Townes and Schawlow³ point out,

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¹ For example, see E. B. Lassetre and L. B. Dean, Jr., *J. Chem. Phys.* **17**, 317 (1948).

² D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).

³ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).