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Microwave Determination of the Structure of Pyrrole

Børge Bak, Daniel Christensen, Lise Hansen, and John Rastrup-Andersen
Chemical Laboratory of the University of Copenhagen, Copenhagen, Denmark

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A number of deuterated pyrroles have been prepared and their microwave spectra recorded. For each isotopic species the two 1→2 transitions observable around 20 000 MHz were localized together with a number of Q-lines in the 17 400–26 000 MHz region scanned. For all isotopic molecules rotational constants were calculated. In this way *seven* mutually independent numerical data were obtained which is insufficient for a direct calculation of the *nine* geometrical parameters of pyrrole. Additional assumptions as to the length of the two C, H bonds lead to definite models for pyrrole.

I. INTRODUCTION

The present microwave work was undertaken as a natural continuation of our previous work on pyridine[1] and furan.[2] Earlier studies of the pyrrole structure by physical methods involves electron diffraction work by Schomaker and Pauling,[3] Raman and infrared spectra by Lord and Miller,[4] and a recent microwave investigation of pyrrole by Wilcox and Goldstein.[5] The electron diffraction work gave 1.395±0.010 A as the average distance between the ring atoms leaving the N, H and C, H distances fully undetermined. Based on this a multitude of models is possible. From the Raman and infrared studies it followed rather unequivocally that pyrrole has C_{2v}-symmetry, but no interatomic distances could, of course, be derived. The microwave investigation[5] served to substantiate Lord and Miller's result. This was done by reference to observed relative intensities of *pairs* of lines, a procedure which does not seem too convincing except in cases where the investigators have cared to demonstrate that complete or comparable separation of the Stark components, belonging to lines, forming a pair, has been achieved.

Ample reasons, therefore, exist for further studies of the pyrrole structure. It may be stated at once that for all six isotopic species investigated here the relationship $I_c = I_a + I_b$ between the principal moments of inertia was found which shows that pyrrole is coplanar in harmony with the theoretical treatment by Coulson and Longuet-Higgins.[6] This excludes that the "classical" chemical formula in which the N, H bond forms an angle with the NC_4-plane, is correct and necessitates a "resonance" or "molecular orbital" description. In what follows the C_{2v}-symmetry of pyrrole will be taken as given. It is the positions of the 10 atoms of pyrrole in the molecular plane which is our problem.

II. EXPERIMENTAL PART

A. Preparation of Materials

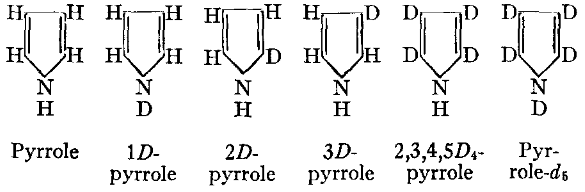
The formulas for pyrrole and the isotopic species studied here are given in Fig. 1.

The preparations were started by providing a stock of high-grade pyrrole, taken from a commercial product by careful distillation through a 50-cm column with glass helices (bp 130.00–130.05°C at 771 mm Hg). The infrared spectrum, recorded on a Beckmann IR2 instrument with NaCl optics in the 670–3500 cm^{-1} region, was shown to be identical with the infrared spectrum of pyrrole, taken by Lord and Miller.[4]

The deuterated pyrroles were made by exchange between samples from the pyrrole-stock and heavy water under varying conditions.

1D-pyrrole: 1 cc pyrrole (0.015 mole) was shaken for 18 hours at 20–25°C with 3 cc D_2O (0.170 mole). Only slight discoloring was observed. After separation from the H_2O-D_2O mixture the 1D-pyrrole sample was dried over anhydrous Na_2CO_3 at 0°C for 1 hour and afterwards distilled under pressure control *in vacuo* at 0°C (where the vapor pressure is about 2 mm) directly into the vessel from which it was admitted to the microwave spectrograph. Yield: 700 mg. The sample was perfectly colorless and transparent. Since only the N-attached hydrogen is exchanged in *neutral* medium we may expect a sample about 95% rich in 1D-pyrrole. The infrared and microwave absorption spectra confirmed that the composition of the sample obtained was about as expected. The dominating lines of the microwave spectrum belonged to a compound with one principal moment of inertia in common with pyrrole as expected for 1D-pyrrole.

Pyrrole-d_5: In *acid* solution all the pyrrole hydrogens are exchanged. 0.1 N D_2SO_4 was prepared from 20 g D_2O



Pyrrole 1D-pyrrole 2D-pyrrole 3D-pyrrole 2,3,4,5D_4-pyrrole Pyrrole-d_5

FIG. 1. Formulas of pyrrole and deuterated pyrroles studied in this paper.

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[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] V. Schomaker and L. Pauling, J. Am. Chem. Soc. 61, 1769 (1939).
[4] R. C. Lord, Jr., and Foil A. Miller, J. Chem. Phys. 10, 328 (1942).
[5] W. S. Wilcox and J. H. Goldstein, J. Chem. Phys. 20, 1656 (1952).
[6] C. A. Coulson and H. C. Longuet-Higgins, Trans. Faraday Soc. 43, 87 (1947).

TABLE I. Observed and calculated microwave absorption frequencies (in MHz) of pyrrole, 1*D*-pyrrole, 3*D*-pyrrole, and pyrrole-d_5 in the 17 400–26 000 MHz region.

Transition	Pyrrole		1*D*-pyrrole		3*D*-pyrrole		Pyrrole-d_5	
(μ_a-lines)	Obs	Calc	Obs	Calc	Obs	Calc	Obs[f]	Calc
$1_{1.1}\rightarrow 2_{1.2}$	22 597.5[a,c]	22 597.6	21 416.3[a]	21 416.3	21 262.1[a]	21 262.2	18 452.2[a]	18 452.1
$1_{0.1}\rightarrow 2_{0.2}$	22 724.1[a,c]	22 724.0	22 099.9[a]	22 099.9	21 964.5[c]	21 964.4	18 520.4[a]	18 520.5
$3_{1.3}\rightarrow 3_{1.2}$	22 657.5[b]	22 657.1	21 427.8[b]	21 428.4	not obs	21 257.8	18 484.5[b]	18 484.2
$3_{0.3}\rightarrow 3_{2.2}$	22 670.9[b]	22 670.9	21 957.1[b]	21 956.6	21 825[b,c]	21 824.7	18 489.3[b]	18 489.1
$4_{2.2}\rightarrow 4_{4.1}$	not obs[d]		18 730.5[b]	18 731.2	not obs	18 894.7	not obs[d]	
$4_{2.3}\rightarrow 4_{2.2}$	22 638.6[b]	22 637.1	20 735[b,c]	20 736.0	20 519.1[b]	20 520.2	18 477.6[b]	18 477.1
$4_{1.3}\rightarrow 4_{3.2}$	22 679.6[b]	22 678.7	22 281.6[b]	22 281.4	22 179[b]	22 175.0	18 491.8[b]	18 491.8
$5_{3.2}\rightarrow 5_{5.1}$	not obs[d]		not obs[e]	22 562.3	22 901.1[b]	22 901.9	not obs[d]	
$5_{3.3}\rightarrow 5_{3.2}$	22 597.5[b,c]	22 597.5	19 540.4[b]	19 540.9	19 256[b]	19 258.2	18 462.7[b]	18 463.1
$5_{2.3}\rightarrow 5_{4.2}$	22 694.1[b]	22 694.7	22 979.6[b]	22 980.1	not obs	22 929.8	18 497.3[b]	18 497.5
$6_{4.3}\rightarrow 6_{4.2}$	22 527.6[b]	22 528.8	17 834.1[b]	17 834.5	17 476.1[b]	17 473.3	18 434.9[c]	18 438.7
$6_{3.3}\rightarrow 6_{5.2}$	22 723.0[b,c]	22 723.4	24 281.6[b]	24 282.6	not obs	24 337.4	18 507.2[b]	18 507.5
$7_{4.3}\rightarrow 7_{6.2}$	22 769.1[b]	22 770.1	not obs[d]		not obs[d]		18 523.1[b]	18 523.7
$7_{5.3}\rightarrow 7_{5.2}$	22 418.8[b]	22 420.3	not obs[d]		not obs[d]		not obs[e]	18 399.8
$8_{6.3}\rightarrow 8_{6.2}$	22 258.8[b]	22 260.6	not obs[d]		not obs[d]		18 339.0[b]	18 341.9
$8_{5.3}\rightarrow 8_{7.2}$	22 840.5[b]	22 841.7	not obs[d]		not obs[d]		18 548.1[b]	18 548.5
$9_{7.3}\rightarrow 9_{7.2}$	22 037.0[b]	22 038.7	not obs[d]		not obs[d]		18 255.7[b]	18 260.1
$9_{6.3}\rightarrow 9_{8.2}$	22 944.6[b]	22 946.0	not obs[d]		not obs[d]		18 584.2[b]	18 584.4
$9_{6.4}\rightarrow 9_{6.3}$	not obs[d]		25 360.5[b]	25 362.2	24 762.6[b]	24 759.9	not obs[d]	
$10_{8.2}\rightarrow 10_{10.1}$	18 537.8[b]	18 538.1	not obs[d]		not obs[d]		not obs[d]	
$10_{8.3}\rightarrow 10_{8.2}$	21 742.3[b]	21 744.7	not obs[d]		not obs[d]		18 143.6[b]	18 149.5
$10_{7.3}\rightarrow 10_{9.2}$	23 090.0[b]	23 092.5	not obs[d]		not obs[d]		18 634.7[b]	18 634.4
$10_{7.4}\rightarrow 10_{7.3}$	not obs[d]		22 743.1[b]	22 745.4	22 010.1[b]	22 009.3	not obs[d]	
$11_{9.2}\rightarrow 11_{11.1}$	19 806.8[b]	19 808.0	not obs[d]		not obs[d]		not obs[d]	
$11_{9.3}\rightarrow 11_{9.2}$	21 368.2[b]	21 370.9	not obs[d]		not obs[d]		17 997.6[b]	18 005.2
$11_{8.3}\rightarrow 11_{10.2}$	23 289.0[b]	23 292.1	not obs[d]		not obs[d]		18 703.1[b]	18 702.3
$11_{8.4}\rightarrow 11_{8.3}$	not obs[d]		19 681.4[b]	19 683.7	18 835.7[b]	18 834.2	not obs[d]	
$12_{10.2}\rightarrow 12_{12.1}$	21 269.9[b]	21 272.1	not obs[d]		not obs[d]		not obs[d]	
$12_{10.3}\rightarrow 12_{10.2}$	20 909.7[b]	20 912.4	not obs[d]		not obs[d]		not obs[d]	
$12_{9.3}\rightarrow 12_{11.2}$	23 553.9[b]	23 557.5	not obs[d]		not obs[d]		not obs[d]	

[a] Unambiguously identified by the Stark effect.
[b] Identified by the "*Q*-line plot" a.s.o. (see text).
[c] Strongly perturbed by adjacent lines.
[d] Outside frequency range investigated.
[e] Small klystron output.
[f] Only investigated in the 18 000–18 750 MHz region.

and 100 mg ordinary conc. H_2SO_4. The hydrogen content of this acid solution is without importance for the present purpose. 2 cc pyrrole was shaken for 1 hour with 2 cc 0.1 N D_2SO_4 after which the acid was removed and substituted by fresh 0.1 N D_2SO_4. After five further repetitions of this procedure the resulting pyrrole-d_5 was separated and purified as above. Yield: 400 mg of a colorless and transparent product. Both microwave and infrared spectra showed that the expected high contents of pyrrole-d_5 had been obtained. An attempt to prepare pyrrole-d_5 from tetraiodopyrrole[7] was also successful, but the yield from 12 g tetraiodopyrrole was only 100 mg. The resulting sample was, however, identical with the "exchange" preparation judging from its vapor pressure and its microwave absorption curve.

2,3,4,5D_4-pyrrole: 400 mg pyrrole-d_5 was shaken for 24 hours with 1 cc H_2O at 20–25°C. The resulting 2,3,4,5D_4-pyrrole was separated, purified etc., as above. Yield: 250 mg of a colorless and transparent product. Its microwave absorption curve showed low contents on pyrrole-d_5 and high contents of a compound with one moment of inertia in common with pyrrole-d_5 as expected for 2,3,4,5D_4-pyrrole.

2D- and 3D-pyrrole: Since we were in possession of samples of *2* and *3D-furan*, it was tried whether the corresponding pyrroles could be obtained by Jurjew's method[8] in which furan is converted to pyrrole by NH_3 at 400°C over Al_2O_3. As might be expected the resulting pyrrole samples were not deuterated as seen immediately from the infrared spectra.

As no other means of attaching deuterium to definite carbon atoms in pyrrole was known to us we had to try to prepare an isotopic mixture reasonably rich in 2*D*- and 3*D*-pyrrole. 0.70 cc pyrrole (0.010 mole) was mixed with 0.115 cc 0.1 N D_2SO_4 (0.00625 mole) and kept at 110°C in a closed vessel for 40 hours. The miscoloring always occurring was somewhat more pronounced here but despite this, 500 mg deuterated pyrroles, colorless and transparent, could be isolated as before. If equilibrium had been established one must expect the sample obtained to consist of about 30% pyrrole, 7.5% 1*D*-

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[7] G. Ciamician and M. Dennstedt, Ber. deut. chem. Ges. **15**, 2582 (1882).

[8] J. K. Jurjew, Ber. deut. chem. Ges. **69**, 1002 (1936).

pyrrole, 15% 2*D*-pyrrole, 15% 3*D*-pyrrole, 20% dideuteropyrroles, and 12.5% higher deuterated pyrroles. The microwave spectrum showed that the pyrrole content had decreased considerably as a consequence of the exchange reaction and that a very large number of "new" lines appeared. The spectrum seemed to be identical with the spectrum of another exchange sample prepared as above but by shorter action of 0.1 N D_2SO_4 on pyrrole at 100°C. Therefore, equilibrium seemed to have been reached. In order to simplify the subsequent spectroscopic work as much as possible the 500 mg exchange sample was shaken for 18 hours with 1.5 cc H_2O, separated from the water a.s.o. as above. 200 mg of a mixture of deuterated pyrroles was isolated. It must be expected to consist of about 37.5% pyrrole, 20% 2*D*-pyrrole, 20% 3*D*-pyrrole, and a mixture (22.5%) of higher deuterated pyrroles *with no deuterium attached to nitrogen*. The infrared absorption curve of the sample showed that strong lines, not to be found in the pyrrole spectrum, appeared besides pyrrole lines considerably reduced in intensity. Very strikingly this infrared spectrum was practically identical with the spectrum of a sample prepared as follows: pyrrole (0.10 mole) was added to CH_3MgJ (0.10 mole) in anhydrous ether. After the evolution of CH_4 had ceased, D_2O (0.50 mole) was added and the ethereal layer removed. The ether was distilled off and the deuterated pyrroles isolated in the usual way. Yield: 2.00 g (30%). This deuterated mixture was shaken with H_2O as above to remove *N*-attached *D*. As mentioned, the infrared spectrum of this sample was about identical with the spectrum of the sample prepared from pyrrole and D_2SO_4. With somewhat less certainty this could also be said of the microwave spectrum (where recorded intensities are not too reliable). The generally accepted idea of the existence of the equilibrium obviously has to be extended to imply the occurrence of molecules with MgHal in the 3-position.

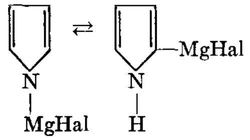

TABLE II. Observed and calculated microwave absorption frequencies (in MHz) for 2*D*- and 2,3,4,5D_4-pyrrole in the 17 400–26 000 MHz region.

Transition (μ_b-lines)	2*D*-pyrrole Obs	2*D*-pyrrole Calc	2,3,4,5D_4-pyrrole Obs	2,3,4,5D_4-pyrrole Calc
$1_{0,1} \rightarrow 2_{1,2}$	22 033.1[a]	22 033.1	19 361.5[a]	19 361.5
$1_{1,1} \rightarrow 2_{0,2}$	21 302.6[a]	21 302.6	18 864.4[a]	18 864.4
$3_{1,3} \rightarrow 3_{2,2}$	21 804.0[b]	21 803.6	19 189.4[b]	19 187.8
$3_{0,3} \rightarrow 3_{1,2}$	21 444.6[b]	21 445.1	18 989.6[b]	18 988.9
$4_{2,3} \rightarrow 4_{3,2}$	not obs	21 994.8	19 294.1[b]	19 294.4
$4_{1,3} \rightarrow 4_{2,2}$	20 977.8[b]	20 978.5	18 719.2[b]	18 720.7
$5_{4,2} \rightarrow 5_{5,1}$	18 208.1[b]	18 208.7	not obs.[d]	
$5_{3,3} \rightarrow 5_{4,2}$	not obs	22 362.8	19 501.5[b]	19 502.1
$5_{2,3} \rightarrow 5_{3,2}$	20 194[b]	20 195.6	18 245.0[b]	18 245.2
$6_{5,2} \rightarrow 6_{6,1}$	20 310.1[b]	20 310.9	not obs.[d]	
$6_{4,3} \rightarrow 6_{5,2}$	22 967.7[b,c]	22 969.3	19 848.7[b]	19 849.4
$6_{3,3} \rightarrow 6_{4,2}$	19 146.1[b]	19 147.9	not obs[d]	
$7_{6,1} \rightarrow 7_{7,0}$	17 845.0[b]	17 845.3	not obs[d]	
$7_{6,2} \rightarrow 7_{7,1}$	22 738.3[b]	22 739.8	18 202.2[b]	18 202.4
$7_{5,3} \rightarrow 7_{6,2}$	23 867.2[b]	23 868.6	20 372.6[b]	20 373.2
$7_{4,3} \rightarrow 7_{5,2}$	18 005.6[b]	18 007.4	not obs[d]	
$8_{7,1} \rightarrow 8_{8,0}$	21 822.2[b]	21 820.7	not obs[d]	
$8_{7,2} \rightarrow 8_{8,1}$	25 454.5[b]	25 456.5	20 117.5[b]	20 117.5
$8_{6,3} \rightarrow 8_{7,2}$	25 099.3[b]	25 101.6	21 104.3[b]	21 105.1
$9_{8,1} \rightarrow 9_{9,0}$	25 888.6[b]	25 887.7	18 975.3[b]	18 974.4
$9_{8,2} \rightarrow 9_{9,1}$	not obs[d]		22 229.1[b]	22 229.4
$9_{7,3} \rightarrow 9_{8,2}$	not obs[d]		22 068.0[b]	22 068.9
$9_{5,4} \rightarrow 9_{6,3}$	not obs[d]		25 135.0[b]	25 137.3
$10_{9,1} \rightarrow 10_{10,0}$	not obs[d]		22 139.2[b]	22 138.6
$10_{9,2} \rightarrow 10_{10,1}$	not obs[d]		24 507.5[b]	24 508.4
$10_{8,2} \rightarrow 10_{9,1}$	20 057.1[b]	20 057.8	not obs[d]	
$10_{8,3} \rightarrow 10_{9,2}$	not obs[d]		23 277.8[b]	23 278.9
$10_{6,4} \rightarrow 10_{7,3}$	25 765.1[b]	25 773.8	24 213.0[b]	24 215.9
$11_{10,1} \rightarrow 11_{11,0}$	not obs[d]		25 278.2[b]	25 278.2
$11_{9,2} \rightarrow 11_{10,1}$	24 001.9[b]	24 002.9	not obs[d]	
$11_{9,3} \rightarrow 11_{10,2}$	not obs[d]		24 737.3[b]	24 738.7
$11_{7,4} \rightarrow 11_{8,3}$	24 184.2[b]	24 188.7	23 081.1[b]	23 084.6
$12_{10,2} \rightarrow 12_{11,1}$	not obs[d]		19 778.1[b]	19 777.0
$12_{9,3} \rightarrow 12_{10,2}$	19 245.1[b]	19 246.9	not obs[d]	
$12_{8,4} \rightarrow 12_{9,3}$	22 784.7[b]	22 790.8	not obs[e]	21 848.7

[a,b,c,d,e] Same meaning as in Table I.

Spectra of asymmetric top molecules are usually very rich in spectral lines. The analysis of a spectrum of a *mixture* of such tops (as we had here) showed to be rather cumbersome, but not impossible, to carry through. Our over-all impression from inspection of the microwave lines finally identified as belonging to either 2*D*- or 3*D*-pyrrole was that perhaps our "exchange sample" was somewhat richer in the 2*D*- than in the 3*D*-isomer, contrary to our expectation. But even then, the concentration of the 3*D*-isomer was sufficiently high for the purpose.

B. Observation and Analysis of the Spectra

The microwave absorption measurements of the vapors of pyrrole and the deuterated species mentioned above were carried out by means of a conventional, Stark-modulated instrument at 20–25°C and at pressures ranging from the generally applied 0.02 mm to 0.001 mm in special cases. Since Goldstein[5] did not measure the pyrrole absorption frequencies to better than 1 MHz the pyrrole microwave spectrum was again studied. The results of our measurements on pyrrole together with the adopted interpretation of the lines (coinciding with Goldstein's analysis) are given in Table I together with corresponding data for 1*D*-, 3*D*-pyrrole and pyrrole-d_5 which obey the same selection rules (μ_a lines). The observations and interpretations pertaining to 2*D*- and 2,3,4,5D_4-pyrrole have been collected in Table II since for these species μ_b lines are observed.

Our general procedure at the analysis was to localize the two 1→2 transitions which we knew must fall somewhere in the 17 400–26 000 MHz region investigated. This phase of the work met with no major difficulties because these transitions are easily recognized due to their very characteristic Stark-pattern. Of course, the possibility exists that these important lines are hidden by some other lines. For pyrrole proper there are lines inconveniently close to both 1→2 transitions, but careful work finally resolved the recorded patterns in which both lines were found and identified by their Stark-effect. Also, the $1_{01}\rightarrow 2_{02}$ transition in the 3*D* spectrum is almost hidden under a very strong, unidentified line at 21 965 MHz (probably a *Q*-line with $J>12$). This circumstance prevented unambiguous identification by means of the Stark-effect. Knowledge of the position of the two 1→2 transitions for a certain species then enabled us to precalculate the approximate localization of a number of *Q*-lines under the assumption that the molecule is coplanar. $E_\tau(\kappa)$ values were taken from Turner's tables. These lines were then sought for and incorporated in our *Q*-line list if they fitted satisfactorily into the usual $\nu_{\mathrm{obs}}/\Delta E(\kappa)$ *versus* κ plot ("*Q*-line plot"). For some of the lines almost resolved Stark-pattern supported the identification. Also, our very large experimental material pertaining to Stark-pattern and experimental intensity of *Q*-lines in isotopic pyridines, furans and pyrroles, including 14 molecules, clearly shows that *Q*-lines may be divided into "families" according to criteria into which we hope to enter in a future publication. The *Q*-lines of the present work formed no exception to the empirical rules found valid for pyridine and furan.

Of course, the analysis of the microwave lines from the "exchange" sample which mainly consists of a mixture of pyrrole, 2*D*- and 3*D*-pyrrole gave extra problems. However, relatively independent of the choice of molecular model *different selection rules* apply for the two monodeuterated species. This means that the two "high-frequency" 1→2 transitions for these species have widely different Stark-patterns. The same is true for the two "low-frequency" lines. Therefore, assignment of 1→2 lines to a definite species offered no special difficulty and since the series of *Q*-lines to be looked for with good approximation follows from the location of these lines (and assumed coplanarity) the *Q*-lines were also identified without too much trouble. The simultaneous presence of at least two other isotopic species was very carefully taken into account in the sense that lines that somehow could be suspected to origin from some other species than the one in question were not included in Tables I and II. Probably some genuine lines have been discarded in this way. As to the internal consistency of the experimental material reference is made to Table III in this paper in which the results of calculating rotational constants in three different ways from our measured lines are shown.

III. CALCULATION OF ROTATIONAL CONSTANTS

In Table III we have summarized the calculated values of the rotational constants, κ etc., derived (1°) from the two 1→2 lines and one of the 3→3 lines;

TABLE III. Calculated values of rotational constants (A,B,C) in MHz, asymmetry parameter (κ), and principal moments of inertia (I_a,I_b,I_c) in amu A² of pyrrole and deuterated pyrroles together with the quantum defect for all six species. Methods of calculation 1°, 2°, 3° according to text.

	Pyrrole			1*D*-pyrrole		
	1°	2°	3°	1°	2°	3°
A	9130.61	9130.46	9130.52	9130.57	9130.55	9130.53
B	9001.23	9001.31	9001.37	8340.71	8340.55	8340.53
C	4532.09	4532.06	4532.12	4358.53	4358.58	4358.56
κ	0.94373	0.94383	0.94383	0.66896	0.66890	0.66890
I_a	55.3610	55.3619	55.3616	55.3613	55.3614	55.3615
I_b	56.1568	56.1563	56.1559	60.6040	60.6051	60.6053
I_c	111.5335	111.5343	111.5328	115.9749	115.9736	115.9741
Q.D.	0.0157	0.0161	0.0153	0.0096	0.0071	0.0073
	2*D*-pyrrole			3*D*-pyrrole		
	1°	2°	3°	1°	2°	3°
A	9018.50	9018.38	9018.37	9088.11	9087.87	9087.93
B	8361.96	8361.87	8361.86	8271.47	8271.52	8271.58
C	4338.20	4338.24	4338.23	4330.21	4330.19	4330.25
κ	0.71945	0.71945	0.71945	0.65672	0.65683	0.65683
I_a	56.0492	56.0500	56.0500	55.6199	55.6214	55.6210
I_b	60.4499	60.4506	60.4507	61.1113	61.1109	61.1105
I_c	116.5184	116.5173	116.5176	116.7334	116.7339	116.7323
Q.D.	0.0193	0.0167	0.0169	0.0022	0.0016	0.0008
	2,3,4,5D_4-pyrrole			Pyrrole-d_5		
	1°	2°	3°	1°	2°	3°
A	7886.29	7885.90	7885.89	7429.58	7429.76	7429.67
B	7429.86	7429.50	7429.49	7360.42	7360.23	7360.14
C	3825.07	3825.20	3825.19	3697.26	3697.32	3697.23
κ	0.77523	0.77521	0.77521	0.96294	0.96274	0.96274
I_a	64.0960	64.0992	64.0993	68.0361	68.0345	68.0353
I_b	68.0336	68.0369	68.0370	68.6754	68.6772	68.6780
I_c	132.1492	132.1447	132.1451	136.7175	136.7152	136.7186
Q.D.	0.0196	0.0086	0.0088	0.0060	0.0035	0.0053

TABLE IV. Possible pyrrole models (I–VI) compatible with the microwave spectra of pyrrole, 1*D*-, 2*D*-, and 3*D*-pyrrole assuming the C, H distances given at the top of the table.

Model No.	I	II	III	IV	V	VI
Distances: C(2), H(2)	1.070	1.080	1.075	1.070	1.080	1.077
C(3), H(3)	1.070	1.080	1.075	1.080	1.070	1.077
N, H(1)	1.008	0.978	0.993	0.993	0.993	0.987
N, C(2)	1.366	1.401	1.383	1.387	1.379	1.391
C(2), C(3)	1.389	1.353	1.371	1.376	1.367	1.364
C(3), C(4)	1.432	1.427	1.429	1.412	1.446	1.428
Angles: C(5)–N–C(2)	110°54′	107°04′	108°56′	109°14′	108°38′	108°08′
N–C(2)–C(3)	107°25′	108°42′	108°05′	107°24′	108°47′	108°21′
C(2)–C(3)–C(4)	107°08′	107°46′	107°27′	107°59′	106°54′	107°35′
N–C(2)–H(2)	122°24′	119°05′	120°42′	120°46′	120°40′	120°01′
H(3)–C(3)–C(4)	126°43′	126°28′	126°36′	126°57′	126°14′	126°33′

(2°) by taking $A-C$ and κ from the Q-line plot (using average values of all points of intersection) and combining with one of the 1→2 lines; (3°) by taking $A-C$ and κ from the Q-line plot and combining with the remaining 1→2 line. The agreement is seen to be satisfactory. In our paper on furan[2] we showed that discrepancies of this order of magnitude between rotational constants have no appreciable effect on the geometrical parameters. Therefore, in what follows mean values of the moments of inertia, calculated in the three different ways, were used.

IV. THE MOLECULAR MODEL

Since the experimental data are insufficient for an unambiguous calculation of the molecular model some assumption has to be made. Just as in our papers on pyridine and furan[1,2] we chose to estimate the length of the two C, H distances. For pyridine, Bastiansen and collaborators[9] showed that the average C, H distance is 1.078±0.005 A. For furan they found the average C, H distance 1.075±0.005 A. This has caused us to consider the six models given in Table IV, all of which equally well explain the microwave spectra of pyrrole, 1*D*-, 2*D*-, and 3*D*-pyrrole. (As to 2,3,4,5D_4-pyrrole and pyrrole-d_5, see later).

From a purely experimental standpoint one cannot get further than to the values given in Table IV. Primitive application of valence theory allows, however, that two of the models are discarded. Pyrrole is a resonance hybrid as shown in Fig. 2.

It is seen that the C(2), C(3) bond is not a simple double bond. Therefore, it must be expected to be somewhat longer than the C, C distance in ethylene (1.353 A). For this reason model II is less probable. On the other hand, one would not expect the resonance to be as complete as in, e.g., benzene. A C(2), C(3) distance close to 1.395 A, the benzene C, C distance, is therefore less probable. Model I, which has a C(2), C(3) distance equal to 1.389 A may therefore be incorrect.

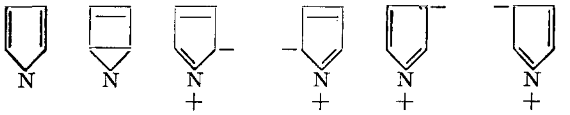

FIG. 2. Conventional resonance components for pyrrole.

It is hard to give a rational choice between the remaining four models. Fortunately, they do not deviate much from each other. Taken as a group they deviate distinctly from the older electron-diffraction picture[3] which had the N, C(2) distance = 1.42 A, the C(2), C(3) distance = 1.35 A, and the C(3), C(4) distance = 1.44 A. The models III–VI agree, however, with the *experimental* result of the electron-diffraction investigation,[3] which gave an average ring-bond length of 1.395 ±0.010 A. For models III–VI this quantity is 1.387–1.388 A.

It is satisfactory to note that models III–VI agree in having 0.987–0.993 A as the N, H distance. The determination is probably the first ever made of the distance from hydrogen to sp^2-hybridized nitrogen. It agrees well with the value 1.014 A found for the distance between hydrogen and sp^3-hybridized nitrogen (NH_3).

The somewhat "odd" model VI was incorporated in Table IV because this model "explains" that the dipole moment of pyrrole is 1.80 *D*[10] and opposite in sign to the dipole moment of pyrrolidine (tetrahydropyrrole) (1.42 *D*) *provided* that the somewhat primitive procedure used for furan[2] is also applied here. The idea of a pyrrole dipole moment being opposite in sign to the tetrahydropyrrole moment is supported by the fact that *N*-methylpyrrole has a ***higher*** dipole moment

TABLE V. Comparison between $I_y^{4C,N}$ and $I_x^{4C,N}$ values (moments of inertia of ring-atoms) found in three different ways (compare text).

	$I_y^{4C,N}$	$I_x^{4C,N}$
From (A)	42.68	43.59
From 2,3,4,5D_4-pyrrole	42.70	43.58
From pyrrole-d_5	42.70	43.56

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[9] Almenningen, Bastiansen, and Hansen, Acta Chem. Scand. 9, 1306 (1955).

[10] Kofod, Sutton, and Jackson, J. Chem. Soc., 1467 (1952).

(1.92 D)[10] than pyrrole itself (1.80 D). Also, the dipole moment of 2,5-dimethylpyrrole is 2.08 D,[10] qualitatively in agreement with our ideas.

A general discussion of the relationship between molecular models for pyridine, furan, pyrrole and thiophene, their dipole moments and chemical properties is, however, postponed to a future publication.

It remains to see how well the models III–VI fit with the experimental results for 2,3,4,5D_4-pyrrole and pyrrole-d_5. Let us define that a y-axis shall go through N and the center of the C(3), C(4) bond, and that the x-axis shall be perpendicular to the y-axis, passing through the center of mass of pyrrole proper. In this coordinate system the coordinates of the hydrogens are fixed independent of the choice of C, H distance (compare references 1 and 2). In these points we now place 4 or 5 D-atoms. I_y^{4D}, the contribution of the deuterium atoms to I_y, is calculated and subtracted from $I_b(=68.0358)$ or $I_a(=68.0353)$. The subtraction will give the quantity $I_y^{4\mathrm{C,N}}$ which must agree with $I_y^{4\mathrm{C,N}}$ derived from the pyrrole, 1D-, 2D-, and 3D-pyrrole data (A). Likewise, $I_x^{4\mathrm{C,N}}$-values found in three different ways are compared in Table V (taking into consideration the displacement of the center of mass).

An error in the hydrogen coordinates amounting to $0.1-0.2\%$ is sufficient to explain the discrepancies.

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Relative Rates of Isomerization of Cyclopropane and Cyclopropane-t_1

R. H. Lindquist* and G. K. Rollefson
Department of Chemistry and Chemical Engineering, University of California, Berkeley, California

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The relative rates of isomerization of cyclopropane and monotritiated cyclopropane have been determined in the temperature range of 447° to 555°C. The ratio of the rate constants for the two reactions can be fitted by the equation:

$$k/k'=0.63\pm0.02\ \exp(825\pm60/RT).$$

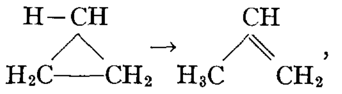
The marked increase in the temperature-independent term upon tritium substitution is discussed in terms of Slater's unimolecular reaction rate theory and Eyring's absolute reaction rate theory. The possibility of classical vibration coupling causing the observed effect is suggested.

INTRODUCTION

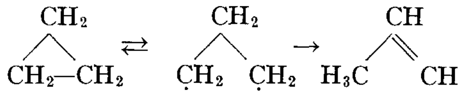
The study of relative rates of reaction of isotopically substituted simple gas phase reactions affords readily interpretable data without conversions and extrapolations for testing reaction rate theories. The validity of proposed mechanisms for the chemical reaction studied can be tested by results of a study of the effect of isotopic substitution on reaction rate.

The isomerization of cyclopropane furnishes a reaction that is homogenous, unimolecular, and the plausible mechanisms of which have been reduced to two.

Chambers and Kistiakowsky[1] proposed both mechanisms; the first a hydrogen disproportionation along a C—C bond with the rupture of a second C—C bond and the doubling of a third:


(1)

the second, a free radical mechanism involving the rupture of a C—C bond as the rate determining step:


(2)

Mechanism (2) was favored by Corner and Pease[2] as a result of their low pressure isomerization experiments. Low pressure experiments by Pritchard, Sowden, and Trotman-Dickenson[3] favor mechanism (1) and cast doubt on the interpretation of Corner and Pease. A complete classical vibrational analysis by N. B. Slater[4] indicated that mechanism (1) was the more plausible.

The relative rates of isomerization of cyclopropane and monotritiated cyclopropane was used as an experimental test of validity of mechanism (1), and of the isotope effect predicted by N. B. Slater's[5] unimolecular reaction rate theory and the effect predicted by H.

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[*] Allied Chemical and Dye Fellow in Physical Chemistry, 1954–1955. Present address: California Research Corporation, Richmond, California.

[1] T. S. Chambers and G. P. Kistiakowsky, J. Am. Chem. Soc. 56, 399 (1934).

[2] E. S. Corner and R. N. Pease, J. Am. Chem. Soc. **67**, 2067 (1945).

[3] Pritchard, Sowden, and Trotman-Dickenson, Proc. Roy. Soc. (London) A217, 563 (1953).

[4] N. B. Slater, Proc. Roy. Soc. (London) **A218**, 224 (1953).

[5] N. B. Slater, Phil. Trans. Roy. Soc. **A246**, 57 (1953).