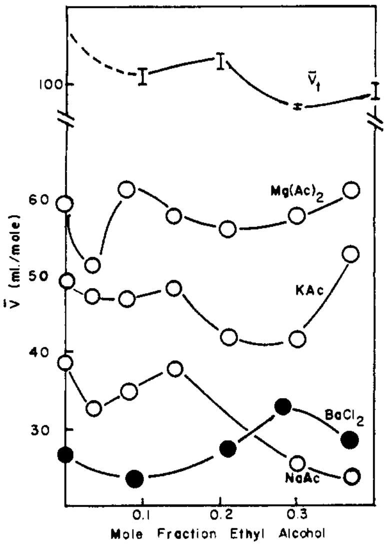

Figure 6. Comparison of the solvent dependence of the partial molal volume of the benzyl chloride solvolytic transition state with various salts in aqueous ethyl alcohol. The acetates are from ref 21 and barium chloride is from ref 20.

coaster" type. The fact that the benzyl chloride transition-state behavior is not unlike that of the electrolytes suggests that it is a pseudo-ionic entity. However, caution must be used in such a comparison. Association of the ions of the salts in the more alcoholic solvents may be great enough to persist to infinite dilution. The partial molal volumes of the salts would therefore be averaged values for the separated ions, undissociated salts, and, in the cases of magnesium acetate and barium chloride, partially ionized species. In pure water, on the other hand, each of the salts undoubtedly exists as dissociated ions. Obviously, the benzyl chloride transition state cannot be described as dissociated ions but may resemble some form of ion pair or highly developed dipole. Therefore, comparison of the transition state with the salts in the highly aqueous solvents must be fortuitous. Nevertheless, the similarity between the partial molal volume behavior of the benzyl chloride solvolytic transition state and each of the salts does suggest that the former is a highly polar species.

In summary, we have found that a minimum in $\Delta V_0^{\ddagger}$ as a function of solvent composition occurs in each of the aqueous alcohol systems studied and is mainly due to the behavior of the partial molal volume of the initial state. The partial molal volume of the transition state shows smaller, but more complex, dependence upon solvent composition than either $\bar{V}_g$ or $\Delta V_0^{\ddagger}$. The behavior of $\bar{V}_t$ for benzyl chloride solvolysis in aqueous ethyl alcohol parallels that of electrolytes, suggesting that the transition state is a highly polar species.

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The Microwave Spectrum and Dipole Moment of Pyrazole

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Contribution from the National Bureau of Standards, Washington, D. C.

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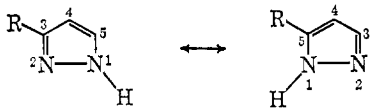
Abstract: The microwave spectrum of pyrazole in the region 8000 to 35,000 Mc/sec has been assigned. The rotational constants are A = 9618.92 ± 0.14, B = 9412.59 ± 0.13, and C = 4755.88 ± 0.11 Mc/sec. The dipole moment, μ = 2.214 ± 0.015 D., was calculated from the Stark effect of the $0_{0,0} \rightarrow 1_{0,1}$ and $0_{0,0} \rightarrow 1_{1,1}$ transitions but only after the perturbation treatment had been extended to fourth order. The indicated uncertainties are three times the standard errors obtained from the least-squares fit. The interpretation of the data shows that in the gas phase pyrazole is a planar molecule with no in-plane symmetry axis.

Although pyrazole is a compound of great chemical interest and has been well studied, very little is known about the physical properties of pyrazole as an isolated molecule. Much of the interest has been concerned with the tautomerism of the pyrazoles substituted in the 3 and 5 positions. These structures are



found to be chemically indistinguishable[1] and, in nuclear magnetic resonance experiments, magnetically equivalent.[2,3] The indistinguishability of the 3- and 5-substituted pyrazoles was first explained by Knorr in 1894, who suggested that the proton was not bonded to just one of the nitrogen atoms but rather oscillated rapidly back and forth between both atoms and, if the temperature could be lowered sufficiently, the oscillation would stop and the two tautomers would become separable isomers.[4] This hypothesis was in fact reasonably close to the currently accepted description

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(1) J. D. Loudon, "Chemistry of Carbon Compounds," Vol. 4, Part A, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1957, p 249.

(2) I. L. Finar and E. F. Mooney, *Spectrochim. Acta*, **20**, 1269 (1964).

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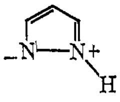
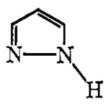
(4) L. Knorr, *Ann. Chem.*, **279**, 188 (1894).

in which the tautomerism results from intermolecular exchange rather than intramolecular exchange. It is now widely accepted on the basis of a large number of physical properties that pyrazole exists in solution as a mixture of monomers and hydrogen-bonded dimers and trimers, although there is still considerable debate concerning the relative abundance of the various species.[3,5–10] The indistinguishability of the 3- and 5-substituted species as well as the magnetic equivalence of the two positions results from cyclic polymerization and subsequent intermolecular proton exchange. There is some evidence that this exchange does not lead to equal distribution of the tautomers but rather that one or the other can predominate, even to the extent of being the sole species present.[11,12] However, this does not negate the mechanism of polymerization and subsequent exchange as the explanation of the tautomerization.

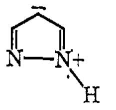
Some interesting results have appeared concerning the structure of pyrazole. From his X-ray analysis, Ehrlich showed that the molecule existed in the crystalline state as a figure-eight helical chain of hydrogen-bonded pyrazole molecules.[13] Depending on its location in the chain, the pyrazole molecule can have two slightly different but definitely distinct geometries. The surprising aspect was that both of these forms could be best represented by the charged structure i rather than the uncharged form ii. Finar and Mooney,[2] from the interpretation of chemical shifts in the nmr spectrum of pyrazole in solution, have indicated a preference for the form iii.



i



ii



iii

Although the nmr evidence for the structure of pyrazole is weaker than that obtained from the X-ray diffraction studies, recent infrared results have indicated that there may be a change in hydrogen bonding when pyrazole is dissolved.[14]

Since the structure of pyrazole determined in the gas phase by microwave spectroscopy is that of an isolated molecule, comparison of this structure with that obtained when the molecule is in a strongly hydrogen-bonded environment gives insight into how much of an effect hydrogen bonding will have on the molecular, and hence electronic, structure of pyrazole. This paper deals with a preliminary investigation of the pyrazole molecule in which the magnitude of the dipole moment is determined and the molecule is shown to be planar, as expected.

The Microwave Spectrum of Pyrazole

In the course of assigning the microwave spectrum of pyrazole, a rather large number of transitions were measured. The subsequently assigned transitions are listed in Table I. Although the assignment of the Q-branch transitions was relatively simple because of their spectral regularity and the large number of such transitions falling in the microwave regions, the assignment of the R-branch transitions was more difficult. The four $J = 1 \rightarrow 2$ transitions expected to fall in the K-band region could not be unambiguously identified by their Stark effect because of the proximity of low J pyrazole Q branch and ammonia transitions (NH_3 was always present as a trace impurity) which led to a confusing Stark-effect pattern. Because the four transitions involved only two pairs of energy levels and hence pairs of transitions sharing common energy levels existed, it was possible to test the assignment by using the technique of double resonance in which the effect of power saturation of one transition is noted in a second transition sharing a common energy level with the first. In particular, the $1_{1,1} \rightarrow 2_{0,2}$ and $1_{1,1} \rightarrow 2_{1,2}$ transitions were saturated, and the effects of this, including the so-called double quantum transitions, were noted in the $1_{0,1} \rightarrow 2_{0,2}$ and $1_{0,1} \rightarrow 2_{1,2}$ transitions.[15] Eventually ten R-branch transitions were observed, thus completing the assignment.

Both *a*- and *b*-type transitions of nearly equal intensity were observed. The spectrum was fit very well by a rigid-rotor pattern with the differences at high values of J being of typical magnitude for centrifugal distortion effects. Broadening and, in some cases, splitting of the spectral lines was observed because of the interaction of the two nitrogen nuclear spins with the over-all rotation of the molecule by means of the nuclear electric quadrupole moments. However, insufficient information was obtained to calculate the magnitude of the coupling constants.

In calculating the rotational constants for pyrazole, 16 transitions involving $J \leq 3$ were fit to rigid rotor formulas by the method of least squares. When a transition exhibiting quadrupole splitting was included in this calculation, the average frequency of the components was used. The rotational constants, moments of inertia, and the inertial defect are given in Table II.

The Dipole Moment of Pyrazole

In order to calculate the dipole moment of pyrazole from the Stark effect of its rotational spectrum, it was necessary to extend the perturbation treatment to fourth order. Golden and Wilson have derived expressions for the Stark effect of a rigid rotor which are correct to second order.[16] They have also shown that the third-order terms vanish identically. Generally, the fourth-order terms are negligible, but pyrazole presents an example where these terms are important.

The rotational energy levels of an asymmetric top in the presence of an electric field are, to fourth order in the electric field

$$W_n = W_n^{(0)} + W_n^{(2)} + W_n^{(4)} \qquad (1)$$

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[15] A. P. Cox, G. W. Flynn, and E. B. Wilson, Jr., *J. Chem. Phys.*, **42**, 3094 (1965).

[16] S. Golden and E. B. Wilson, Jr., *ibid.*, **16**, 669 (1948).

Table I.[a] The Microwave Spectrum of Pyrazole

Transition	Frequency	Obsd − calcd
$1_{0,1} \rightarrow 0_{0,0}$	14167.24	−1.24
	14168.62	+0.14
$1_{1,1} \rightarrow 0_{0,0}$	14374.57	−0.23
	14375.41	+0.61
$2_{0,2} \rightarrow 1_{1,1}$	23673.24	−0.33
$2_{1,2} \rightarrow 1_{1,1}$	23679.94	−0.34
$2_{0,2} \rightarrow 1_{0,1}$	23880.05	+0.15
$2_{1,2} \rightarrow 1_{0,1}$	23886.86	+0.26
$2_{1,1} \rightarrow 1_{1,0}$	32993.63	−0.01
$2_{2,0} \rightarrow 1_{0,1}$	42932.47	−0.19
	42933.51	−0.85
$3_{0,3} \rightarrow 2_{1,2}$	33290.59	−0.39
$3_{1,3} \rightarrow 2_{1,2}$		−0.53
$3_{1,3} \rightarrow 2_{0,2}$	33297.32	−0.50
$3_{0,3} \rightarrow 2_{0,2}$		−0.36
$2_{1,1} \rightarrow 2_{1,2}$	13970.22	+0.18
$2_{1,1} \rightarrow 2_{0,2}$	13976.73	−0.02
$2_{2,1} \rightarrow 2_{1,2}$	14588.65	−0.35
	14589.91	+0.91
$2_{2,1} \rightarrow 2_{0,2}$	14595.42	−0.29
$3_{2,1} \rightarrow 3_{2,2}$	13664.34	−0.48
	13665.27	+0.45
$3_{2,1} \rightarrow 3_{1,2}$	13697.84	−0.46
	13698.75	+0.45
$3_{3,1} \rightarrow 3_{2,2}$	14901.64	−0.96
	14903.17	+0.57
$3_{3,1} \rightarrow 3_{1,2}$	14934.78	−1.30
	14935.32	−0.76
	14936.82	+0.74
$3_{1,2} \rightarrow 3_{1,3}$	23768.9	−1.1, +0.1
$3_{1,2} \rightarrow 3_{0,3}$	23770.1	−1.0, +0.2
$3_{2,2} \rightarrow 3_{1,3}$	23802.18	−1.14, +0.23
$3_{2,2} \rightarrow 3_{0,3}$	23803.55	−1.28, +0.09
$4_{3,1} \rightarrow 4_{3,2}$	13260.59	−0.20
	13261.30	+0.51
$4_{3,1} \rightarrow 4_{2,2}$	13360.57	−0.20
	13361.30	+0.51
$4_{2,2} \rightarrow 4_{2,3}$	23721.4	−0.1
$4_{2,2} \rightarrow 4_{1,3}$	23722.3	−0.1
$4_{3,2} \rightarrow 4_{2,3}$	23821.32	−0.23
$4_{3,2} \rightarrow 4_{1,3}$	23822.25	−0.25
$4_{1,3} \rightarrow 4_{1,4}$	33305.74	−0.27, −0.08
$4_{1,3} \rightarrow 4_{0,4}$	33305.93	−0.27, −0.08
$4_{2,3} \rightarrow 4_{1,4}$	33306.90	−0.06, +0.28
$4_{2,3} \rightarrow 4_{0,4}$	33306.68	−0.06, +0.28
$5_{3,2} \rightarrow 5_{3,3}$	23625.4	−0.6
$5_{3,2} \rightarrow 5_{2,3}$	23629.2	−0.6
$5_{4,2} \rightarrow 5_{3,3}$	23857.34	−0.75
$5_{4,2} \rightarrow 5_{2,3}$	23861.10	−0.80
$5_{2,3} - 5_{2,4}$	33295.74	−0.66, −1.45
$5_{2,3} - 5_{1,4}$	33294.95	−0.68, −1.47
$5_{3,3} - 5_{2,4}$	33299.61	−0.60, −1.47
$5_{3,3} - 5_{1,4}$	33298.74	−0.62, −1.49
$6_{5,1} \rightarrow 6_{5,2}$	12168.73	−0.58
	12169.81	+0.50
$6_{4,2} \rightarrow 6_{4,3}$	23461.5	−0.7
$6_{4,2} \rightarrow 6_{3,3}$	23472.9	−0.7
$6_{5,2} \rightarrow 6_{4,3}$	23920.4	−1.0
$6_{5,2} \rightarrow 6_{3,3}$	23931.6	−1.2
$6_{3,3} \rightarrow 6_{3,4}$[b]	33277.38	−1.03
$6_{3,3} \rightarrow 6_{2,4}$[b]		−1.14
$6_{4,3} \rightarrow 6_{3,4}$	33288.74	−1.08
$6_{4,3} \rightarrow 6_{2,4}$		−1.18
$7_{6,1} \rightarrow 7_{6,2}$	11491.29	−0.40
	11492.41	+0.52
$7_{5,2} \rightarrow 7_{5,3}$	23206.8	−0.9
$7_{5,2} \rightarrow 7_{4,3}$	23235.0	−1.1
$7_{6,2} \rightarrow 7_{5,3}$	24019.4	−1.5
$7_{6,2} \rightarrow 7_{4,3}$	24047.9	−1.4
$7_{4,3} \rightarrow 7_{4,4}$	33245.60	−1.61
$7_{4,3} \rightarrow 7_{3,4}$	33245.95	−1.64
$7_{5,3} \rightarrow 7_{4,4}$	33273.93	−1.69
$7_{5,3} \rightarrow 7_{3,4}$	33274.31	−1.69
$8_{7,1} \rightarrow 8_{7,2}$	10735.98	−0.56
	10737.07	+0.53
$8_{7,1} \rightarrow 8_{6,2}$	12060.24	−0.89
$8_{7,2} \rightarrow 8_{6,3}$	24164.7	−2.0
$8_{7,2} \rightarrow 8_{5,3}$	24266.6	−2.3
$8_{5,3} \rightarrow 8_{5,4}$	33193.79	−2.26
$8_{5,3} \rightarrow 8_{4,4}$	33194.93	−2.25
$8_{6,3} \rightarrow 8_{5,4}$	33255.98	−2.38
$8_{6,3} \rightarrow 8_{4,4}$	33257.06	−2.35
$9_{9,0} \rightarrow 9_{8,1}$	10840.9	−3.1
	10842.53	−1.45
$9_{8,1} \rightarrow 9_{8,2}$	9913.24	−0.49
	9914.22	+0.49
$9_{8,1} \rightarrow 9_{7,2}$	11931.70	−1.43
$9_{8,2} \rightarrow 9_{7,3}$	24366.5	−2.7
$9_{8,2} \rightarrow 9_{6,3}$	24489.8	−2.9
$9_{6,3} \rightarrow 9_{6,4}$	33112.97	−2.89
$9_{6,3} \rightarrow 9_{5,4}$	33115.95	−2.86
$9_{7,3} \rightarrow 9_{6,4}$	33236.40	−3.04
$9_{7,3} \rightarrow 9_{5,4}$	33239.31	−3.07
$10_{9,1} \rightarrow 10_{9,2}$	9036.2	−0.6
	9037.2	+0.4
$10_{9,2} \rightarrow 10_{8,3}$	24635.1	−3.4
$10_{9,2} \rightarrow 10_{7,3}$	24861.9	−3.9
$10_{7,3} \rightarrow 10_{7,4}$	32991.30	−3.49
$10_{7,3} \rightarrow 10_{6,4}$	32998.10	−3.53
$10_{8,3} \rightarrow 10_{7,4}$	32218.24	−3.86
$10_{8,3} \rightarrow 10_{6,4}$	33225.11	−3.84
$11_{10,1} \rightarrow 11_{9,2}$	12148.83	−2.65
$11_{10,2} \rightarrow 11_{9,3}$	24980.3	−4.2
$11_{10,2} \rightarrow 11_{8,3}$	25372.3	−4.8
$11_{8,3} \rightarrow 11_{8,4}$	32813.88	−4.14
$11_{8,3} \rightarrow 11_{7,4}$	32828.44	−4.17
$11_{9,3} \rightarrow 11_{8,4}$	33205.87	−4.74
$11_{9,3} \rightarrow 11_{7,4}$	33220.47	−4.73
$12_{11,2} \rightarrow 12_{10,3}$	25411.3	−4.9
$12_{9,3} \rightarrow 12_{9,4}$	32563.04	−4.74
$12_{9,3} \rightarrow 12_{8,4}$	32591.92	−4.85
$12_{10,3} \rightarrow 12_{9,4}$	33205.10	−5.68
$12_{10,3} \rightarrow 12_{8,4}$	33234.01	−5.76
$13_{13,1} \rightarrow 13_{12,2}$	24026.2	−3.6
	24027.5	−2.3
$13_{12,2} \rightarrow 13_{11,3}$	25936.2	−5.5
$13_{10,3} \rightarrow 13_{10,4}$	32218.71	−5.46
$13_{10,3} \rightarrow 13_{9,4}$	32272.98	−5.63
$13_{11,3} \rightarrow 13_{10,4}$	33223.14	−6.77
$13_{11,3} \rightarrow 13_{9,4}$[b]	33277.38	−6.96
$14_{14,1} \rightarrow 14_{13,2}$	25508	−4
	25509.5	−2.3
$14_{11,3} \rightarrow 14_{11,4}$	31760.16	−6.14
$14_{11,3} \rightarrow 14_{10,4}$	31856.95	−6.46
$14_{12,3} \rightarrow 14_{11,4}$	33268.53	−8.00
$15_{12,3} \rightarrow 15_{12,4}$	31167.51	−6.96
$15_{12,3} \rightarrow 15_{11,4}$	31332.88	−7.40
$16_{13,3} \rightarrow 16_{13,4}$	30424.68	−7.85
$16_{13,3} \rightarrow 16_{12,4}$	30695.97	−9.12
	30696.37	−8.72
$17_{16,2} \rightarrow 17_{14,3}$	33230.96	−10.35
	33229.32	−11.99
$17_{14,3} \rightarrow 17_{14,4}$	29520.99	−8.89
	29520.35	−9.53
$17_{14,3} \rightarrow 17_{13,4}$	29952.32	−10.34
	29952.82	−9.84
$18_{15,3} \rightarrow 18_{15,4}$	28453.28	−10.10
	28452.52	−10.86
$18_{15,3} \rightarrow 18_{14,4}$	29118.13	−11.30
$19_{17,2} \rightarrow 19_{17,3}$	11246.22	−7.31
	11247.09	−6.44
$19_{18,2} \rightarrow 19_{17,3}$	31316.11	−9.14
	31316.89	−8.36
$19_{16,3} \rightarrow 19_{16,4}$	27225.70	−11.46
$19_{16,3} \rightarrow 19_{15,4}$	28220.01	−13.08
$20_{19,1} \rightarrow 20_{18,2}$	24210.7	−3.6
	24211.8	−2.5
$20_{18,2} \rightarrow 20_{18,3}$	9872.38	−8.00
	9873.16	−7.22

Table I (*Continued*)

Transition	Frequency	Obsd − calcd	Transition	Frequency	Obsd − calcd
$20_{17.3} \rightarrow 20_{16.4}$	27296.50	−15.00	$24_{21.3} \rightarrow 24_{20.4}$	24307	−23
$21_{20.1} \rightarrow 21_{19.2}$	26575.32	−2.49	$25_{22.3} \rightarrow 25_{21.4}$	23980	−23
$21_{18.3} \rightarrow 21_{18.4}$	24339.9	−15.0	$28_{25.3} \rightarrow 28_{25.4}$	12063.28	−29.41
$22_{19.3} \rightarrow 22_{18.4}$	25559.8	−19.1		12064.01	−28.68
$23_{20.3} \rightarrow 23_{19.4}$	24848.2	−20.9	$29_{26.3} \rightarrow 29_{26.4}$	10400.62	−30.76
$24_{22.2} \rightarrow 24_{21.3}$	23233.0	−9.1		10401.27	−30.11
	23233.7	−8.4			

[a] In some cases quadrupole fine structure was resolved and all measured components are reported. The possibility always exists that the structure may not be due to quadrupolar interactions but merely to the presence of a high J transition falling close to the assigned transition. All frequencies are in Mc/sec. For those frequencies reported to a precision of 0.01 Mc/sec, the experimental uncertainty is ±0.1 Mc/sec; for those reported to a precision of 0.1 Mc/sec, the uncertainty is ±0.5 Mc/sec; for those reported to a precision of 1 Mc/sec, the uncertainty is ±1 Mc/sec. Occasionally two transitions will not be resolved and they appear in the table bracketed together. Of these transitions, several show hyperfine structure and the deviations of the components from the calculated frequency of each transition are included on the same line as the assignment. The obsd − calcd values are the differences of the observed frequencies from the rigid rotor frequencies calculated using the rotational constants in Table II. [b] The $13_{11.3} \rightarrow 13_{9.4}$, $6_{3.3} \rightarrow 6_{2.4}$, and $6_{3.3} \rightarrow 6_{3.4}$ transitions are all coincident.

Table II. Rotational Constants and Principal Moments of Inertia of Pyrazole[a]

$A = 9618.92 \pm 0.14$ Mc/sec[b]
$B = 9412.59 \pm 0.13$ Mc/sec
$C = 4755.88 \pm 0.11$ Mc/sec
$I_a = 52.5398 \pm 0.0008$ uA^2
$I_b = 53.6915 \pm 0.0007$ uA^2
$I_c = 106.2634 \pm 0.0025$ uA^2
$\Delta = I_c - (I_a + I_b) = +0.0321 \pm 0.0027$ uA^2

[a] Conversion factor $hN_a/8\pi^2 = 505{,}376$ uA^2 Mc/sec where 1 u = 1 unified atomic mass unit = $^1/_{12}$ the mass of the ^{12}C nuclide. [b] The uncertainties quoted here are three times the standard errors obtained from the least-squares fit.

where $W_n^{(0)}$ is the unperturbed energy

$$W_n^{(2)} = \sum_m{}' \frac{|V_{nm}|^2}{W_n^{(0)} - W_m^{(0)}} \qquad (2)$$

and

$$W_n^{(4)} = \sum_l{}' \frac{1}{W_n^{(0)} - W_l^{(0)}} \left| \sum_m{}' \frac{V_{nm}V_{ml}}{W_n^{(0)} - W_m^{(0)}} \right| - W_n^{(2)} \sum_m{}' \frac{|V_{nm}|^2}{(W_n^{(0)} - W_m^{(0)})^2} \qquad (3)$$

Here the perturbation $V = -\vec{\mu} \cdot \vec{E}$; the matrix elements V_{nm} are those of the operator V in the basis set formed of the unperturbed rigid rotor eigenfunctions; the indices n, m, and l stand for the set of quantum numbers which specify each rotational eigenstate; and the summations extend over all states except n. The expression for $W_n^{(4)}$ was derived by making use of the fact that $V_{mn} = V_{nm}^*$ and $V_{nn} = 0$.

An easily usable expression for $W_n^{(2)}$ can be derived by relating the absolute values of the matrix elements V_{nm} to the transition line strengths which are readily available in tabular form.[17] This is not possible for $W_n^{(4)}$ which requires evaluation of the individual matrix elements V_{nm} instead of only their absolute values. Now

$$V = -\vec{\mu} \cdot \vec{E} = -E \sum_{g = a,b,c} \Phi_{Zg}\mu_g$$

where the electric field E has been arbitrarily taken to lie along the Z axis. Φ_{Zg}'s are the direction cosines of the molecule-fixed principal axes along the space-fixed Z axis, and μ_g is the component of μ along the gth principal axis. V_{nm} can be calculated once the expectation values of the Φ_{Zg} in the asymmetric rotor basis have been evaluated, and these in turn can be calculated from the scheme of King, Hainer, and Cross.[18] The evaluation of $W_n^{(4)}$ is thus quite straightforward but tedious. For low values of J, the number of terms appearing in eq 3 is manageable.

Pyrazole is a near-oblate top and hence has energy levels which are nearly degenerate, namely, the K-type doublets which are exactly degenerate in the symmetric top limit. Matrix elements of V between these levels vanish because the component of the molecular dipole moment perpendicular to the plane of the molecule is identically zero. Thus, no effect of these near degeneracies is noted in second order where the small energy denominators are accompanied by vanishing numerators. However, in the first term in eq 3 it can be seen that the energy difference $W_n^{(0)} - W_l^{(0)}$ appears with no corresponding term V_{nl} in the numerator. Instead, the state n is "connected" to the state l by means of a third state, or, for higher eigenstates, by means of several third states. Without going into detail, it is found from the transformation properties of the rigid rotor wave functions and the perturbation operator V that in order for the K-type doublets to contribute to the fourth-order terms, the a and b components of the dipole moment must both be nonvanishing. Qualitatively, if n and l represent a K-type doublet for a near-oblate top, they are connected by μ_c. In order that they may be connected by a third state m, n must be connected to m by μ_a and m to l by μ_b (or *vice versa*). The existence of both a- and b-type transitions in pyrazole showed that μ_a and μ_b were both appreciable. Thus, it was suspected that there might be significant fourth-order contributions to the Stark effect.

The Stark effects of the $0_{0,0} \rightarrow 1_{0,1}$ and $0_{0,0} \rightarrow 1_{1,1}$ transitions in pyrazole were measured in a conventional Stark cell using a high-precision dc voltage supply. Sufficient square-wave voltage was superimposed on top of the dc voltage to modulate the transitions, and the average of both components was measured. This procedure ensures that the relatively large uncertainties in the square-wave voltage do not contribute signifi-

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(18) P. C. Cross, R. M. Hainer, and G. W. King, *J. Chem. Phys.*, 12, 210 (1944).

cantly to the accuracy of the voltage measurements. Since the conventional Stark cell differs significantly from an ideal parallel plate capacitor, broadening of the transitions was observed due to inhomogeneities in the electric field, and it was found that it was not practical to measure Stark shifts greater than 50 or 60 Mc/sec. The effective guide spacing was calculated by measuring the Stark effect of OCS and using the Marshall and Weber value of the dipole moment, 0.7124 ± 0.0002 D.[19] The frequencies of the Stark components were measured at 10 to 15 values of the electric field, and the data were fit by the method of least squares to the slope and intercept of a quadratic function of the voltage. Quartic effects, that is, effects due to the fourth-order Stark shifts, were included in both the OCS calibration and the pyrazole measurement using an iterative scheme whereby the effective guide spacing (in OCS) or dipole moment (in pyrazole) was first calculated assuming no quartic effects. The quartic contribution was then calculated and subtracted from the observed frequency shifts, and these corrected shifts were again fit to a quadratic equation. Only one such iteration was necessary. In measuring the Stark effect of pyrazole, the pressure was kept high enough that the quadrupole fine structure was not resolved.

In carrying out the least-squares fit, the transitions were weighted by the inverse square of the applied voltage. This was done because at higher voltage the lines were broadened, thus causing the uncertainty in frequency measurement to be greater than at lower voltages. The broadening, and hence uncertainty, was proportional to the magnitude of the total shift and hence to the square of the applied voltage.

Before calculating the fourth-order contribution to the Stark effect in pyrazole, the data were first fit to a quartic function of the applied voltage. The value of the quartic term obtained was $-0.72 \pm 0.25 \times 10^{-12}$ (Mc/sec)/(v/cm)^4 for the $0_{0,0} \rightarrow 1_{0,1}$ transition and $+0.75 \pm 0.55 \times 10^{-12}$ (Mc/sec)/(v/cm)^4 for the $0_{0,0} \rightarrow 1_{1,1}$ transition. The large uncertainties indicate that the values were poorly determined, but, since terms of this magnitude should contribute as much as 5% of the total Stark shift at high voltages, it indicated that the fourth-order effects were important and should be included. Using the value of the dipole moment calculated by fitting the frequency shifts to a quadratic function of the voltage, the fourth-order contribution to the Stark shifts calculated from eq 3 was found to be -0.990×10^{-12} (Mc/sec)/(v/cm)^4 for the $0_{0,0} \rightarrow 1_{0,1}$ transition and $+0.859 \times 10^{-12}$ (Mc/sec)/(v/cm)^4 for the $0_{0,0} \rightarrow 1_{1,1}$ transition. The agreement with the experimentally determined values is surprisingly good.

With inclusion of the fourth-order effects, the calculated values of the dipole moment and the components of the dipole moment along the principal axes are $\mu_a = 1.640 \pm 0.013$ and $\mu_b = 1.488 \pm 0.021$ D. and $\mu = 2.214 \pm 0.010$ D., where the uncertainties in these quantities are taken to be twice the standard deviation obtained from the least-squares fit. Had the quartic contribution to the Stark effect been ignored, the values obtained would have been $\mu_a = 1.541$, $\mu_b = 1.581$, and $\mu = 2.208$ D., showing that the effect is quite important for μ_a and μ_b but not for μ itself.

Although μ_a and μ_b have been obtained, the orientation of the dipole moment in the molecule is not known because the orientation of the principal axes themselves is not known. Only when further structural information is obtained can the orientation of the dipole moment be found.

Discussion

The size of the inertial defect given in Table II, $\Delta = +0.0321$ uA^2, has the typical magnitude and sign found in planar ring compounds and indicates that pyrazole is indeed a planar molecule.[20] Furthermore, existence of a dipole moment component along both the *a* and *b* principal axes shows that there is no symmetry axis in the plane of the molecule. Such an axis would occur if the nitrogenous proton was shared between both nitrogens or was oscillating very rapidly ($>10^6$ times/sec) between them. This supports the argument that the chemical and magnetic equivalence of the 3 and 5 positions is due to intermolecular rather than intramolecular exchange.

Further comments on the structure of pyrazole are not possible using the information obtained from the rotational spectrum of only the most prevalent isotopic species. In order to obtain a quantitative structure it is necessary to observe and assign the spectrum of several other isotopic species. Such a study is currently under way in another laboratory.

Two dielectric measurements have been made of the dipole moment of pyrazole in solution.[21,22] In benzene solution, Jensen and Friediger obtained a dipole moment of 1.57 D. while Hückel and Salinger obtained a value in dioxane ranging from 2.02 to 2.46 D., depending on the temperature and concentration. From molecular weight determinations, Jahnetz and Hückel[23] concluded that the degree of association of pyrazole was greater by an order of magnitude in benzene than in dioxane so that, even though the experimental procedure of Jensen and Friediger was more reliable, the high degree of association of pyrazole in benzene led, on extrapolation to infinite dilution, to a value which was too low. The value of Hückel and Salinger is in rather good agreement with the microwave value of 2.214 ± 0.010 D. The microwave value also differs significantly from the value of 1.50 D. calculated by Hamano and Hameka.[24] Hence, the predictions which they made on the basis of their calculated charge distribution may have to be modified.

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