The Vibration Spectra and Electric Moments of Azomethane, N–N′ Dimethylhydrazine and Acetaldazine

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The investigations reported here on azomethane, $CH_3 \cdot N = N \cdot CH_3$, N—N' dimethyl-hydrazine, $(CH_3)HN \cdot NH(CH_3)$, and acetaldazine $(CH_3)HC = N - N = CH(CH_3)$ were carried out primarily to obtain information on the general form and some of the structural properties of these molecules, which are of a type whose chemical behavior with respect to thermal and photodecomposition is of considerable current interest. The properties examined have included the Raman spectra, with the state of polarization of the stronger lines, in the liquid state, and the electric moment in solution of the three compounds; the infrared absorption spectrum of azomethane vapor has also been investigated to the degree possible with the resolution ordinarily obtained from a rocksalt prism spectrometer.

THE electron diffraction pattern of azomethane, studied by H. Boersch,[1] indicates a C — N distance of 1.47 ± 0.06A and a N — N distance of 1.24 ± 0.05A, the former distance being the normal single bond C — N distance, and the other nearly the normal double bond N — N distance.[2]

The patterns did not permit an unambiguous differentiation between the *cis* and *trans* arrangements of the methyl groups in the molecule (or even a definite exclusion of a nonplanar form), but did eliminate the linear arrangement of carbon and nitrogen atoms, and, arguing from the absence of a permanent electric moment in azobenzene, Boersch concludes that the trans-planar model is the best representation of azomethane. To anticipate our experimental results, the Raman and infrared spectra we have found exhibited by azomethane are in fact those of a

molecule possessing a symmetry center, which, along with the zero moment the substance is found to have in heptane solution, and Boersch's elimination of the linear model, indicate conclusively a *trans* arrangement of the methyl groups in the azomethane molecule.

The structure of the hydrazines becomes particularly interesting in view of the conclusion of Penney and Sutherland[3] as to the strong asymmetry of hydrazine. Like that of hydrazine, the Raman spectrum of N — N' dimethylhydrazine is that characteristic of an asymmetric molecule, and the electric moment in heptane solution is distinctly greater than zero. Assuming a skeleton for dimethylhydrazine similar to that proposed by Penney and Sutherland for hydrazine, one finds three possible isomers for the compound, of different theoretical electric moments, of which one is found to be in good agreement with the observed moment.

[1] H. Boersch, Monatsch. **65**, 311 (1935).
[2] L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).

[3] W. G. Penney and G. B. B. M. Sutherland, Trans. Faraday Soc. **30**, 898 (1934). J. Chem. Phys. **2**, 492 (1934).
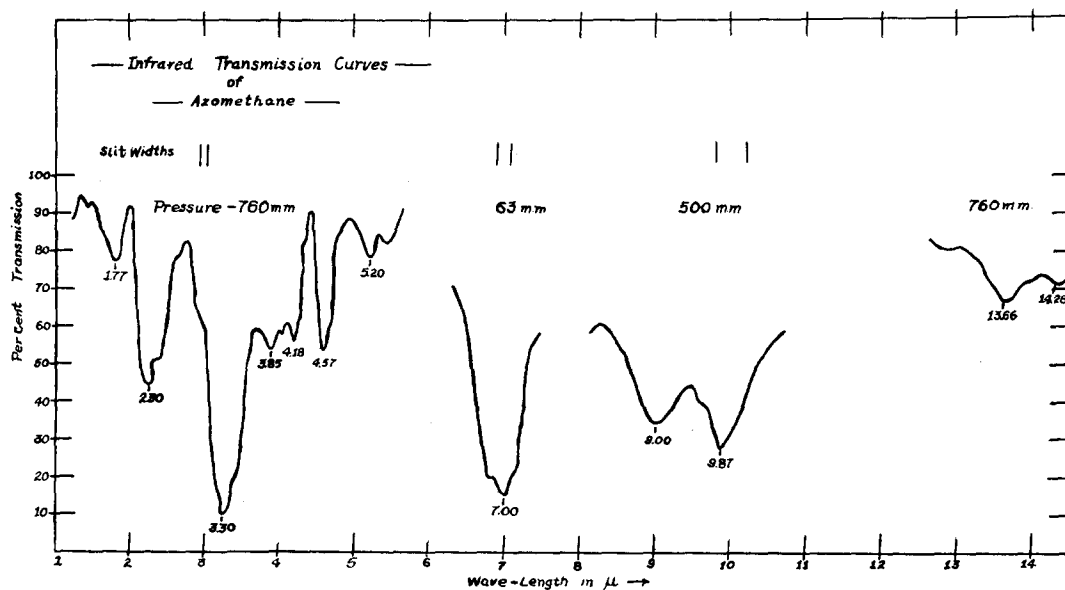
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FIG. 1.

EXPERIMENTAL PROCEDURE

Dimethylhydrazine hydrochloride, required for the preparation of dimethylhydrazine and azomethane, was prepared by the method of Hatt.[4]

From this the base was liberated by the action of sodium hydroxide solution, in an apparatus connected to a vacuum line, due precautions (refluxing over barium oxide) being taken to remove water. The final distillation was directly into the Raman cell. The color, b.p. (80.5°), density (0.827), and refractive index (1.4201 for D) indicated high purity.

Azomethane was prepared by oxidation of dimethylhydrazine hydrochloride by Thiele's method,[5] purified by fractional distillation at $-80°C$ through condensers cooled by dry ice into receivers in liquid air, and finally distilled as a colorless liquid into the Raman cell cooled by dry ice. Between exposures, azomethane, b.p. 1.5°C was allowed to evaporate into a large evacuated flask connected to the Raman cell to prevent the accumulation of pressures above atmospheric of this explosive compound.

Acetaldazine was prepared from acetaldehyde and hydrazine hydrate by the method of Curtius.[6]

[4] H. H. Hatt, *Organic Synthesis*, Vol. 16 (John Wiley and Sons, Inc., New York, 1936), p. 18.
[5] J. Thiele, Ber. 42, 2576 (1909).
[6] T. Curtius, J. Prak. Chem. 58, 325 (1898).

Raman spectrum

Filtered mercury radiation, 4358A and 4047A, was used to photograph the spectra; the dispersion was 90 cm^{-1} per mm at 4400A. Since azomethane was found to absorb in the near ultraviolet with the production of a crystalline solid, the scattering for wave-length 4358A was alone investigated in this case.

The small volume of the Raman cell (3 cc) made rather long exposures necessary, during which, in experiments on azomethane, the accumulation of frost on the cell or Dewar had to be prevented. A sheet metal box, into which the Raman cell fitted, was mounted rigidly in the Dewar, with the necessary passages for entry and exit of light sealed air-tight to the inner wall of the Dewar by moulding plaster, and provided with desiccant. A glass tube with window, mounted in the same way on the outer wall towards the spectrograph kept the passage of the scattered light clear, while a fan directed on the place of incidence of the exciting light on the outer wall prevented frosting here.

To measure the depolarization factors of the scattered lines, a Wollaston prism was placed in front of the camera lens and the densities of the double spectrum measured by a Moll microdensitometer, due regard being taken to ensure parallelism of the incident light by passing it

through vertical slots,[7] and to avoid spurious reflections. On the same plate intensity marks were made by photographing the spectrum of an incandescent bulb of accurately known variable intensity also resolved into perpendicular and parallel components by the Wollaston. A calibration curve showing the relation between light intensity and photographic density was made, and at the same time the correction to be applied owing to the greater loss by reflection at the surfaces of the optical parts of the spectrograph of the vertical component of the light was found. The degree of depolarization of the Raman lines of CCl_4 evaluated in this way agreed to within 0.03 with the values of Cabannes and Rousset.[8]

Infrared spectrum

The infrared absorption spectrum of azomethane was measured by use of a rocksalt prism instrument with a 60° prism of 5 cm base, mirrors at $f:6$ and 36 cm focal length, a Moll linear thermopile and Leeds and Northrup H.S. low resistance galvanometer. A globar served as source. The absorption cell was 20 cm long, with rocksalt windows. The pressures of azomethane used are indicated in the curve (Fig. 1).

Dielectric constant measurements

The dielectric constants of solutions of the substances in n-heptane were measured by the heterodyne method at a frequency of 3.5×10^6 c.p.s. The oscillator was built by Dr. R. L. Garman of this department, and was essentially similar to that described by Stranathan,[9] in which the chief feature is the almost complete elimination, by adequate shielding and temperature control, of frequency drift. In view of the relatively high frequency used, special precautions were made to eliminate inductance errors introduced by the leads by exact mechanical as well as electrical substitution of the measuring cell for the standard condenser. The dielectric cell was calibrated against benzene, dielectric constant 2.279, and ether, dielectric constant 4.240, both at 25°C.

The cell, of the general design of Smyth and Morgan,[10] held 6 cc of solution. The method of filling the cell with azomethane solution of known composition should perhaps be described in a little detail. A weighed glass trap, provided with a side arm with stopcock, and with a capillary syphon reaching to the bottom, was attached, after the introduction of a weighed amount of heptane, by means of the side tube to the vacuum line used for the generation of azomethane. The trap was immersed in liquid air, with consequent freezing of the heptane, evacuated, and solid azomethane allowed to condense on the heptane, in which it dissolved when the temperature was allowed to rise. The weight of the solution was determined and the composition ascertained. To transfer the solution to the dielectric cell, the capillary syphon was connected to the cell by a ground joint and the solution carefully pushed over by means of dry air.

Densities were determined in a 1 cc pyknometer and refractive indices conveniently measured by squirting a few drops of solution from a medicine dropper through the drainage

TABLE I. *Vibration spectrum of azomethane.*

RAMAN (LIQUID) AT −60°C			INFRARED (GAS) AT 20°C	
$\Delta\bar\nu(cm^{-1})$	I	ρ_n	$\lambda(\mu)$	$\bar\nu(cm^{-1})$
548	1			
596	8	0.3		
			14.28	700
			13.66	730
922	4			
1023	1		9.87	1013
			9.00	1110
1182	3			
1376	5	$D*$		
1442	9	.6	7.00	1430
1576	4			
			5.20	1923
			4.57	2190
			4.18	2392
			3.85	2597
2733	2			
2854	2			
2914	10	.25		
2985	8	D		
			3.30	3030
			2.30	4360
			1.77	5650

* D indicates a line too feeble to permit an accurate estimation of ρ_n but which was strongly depolarized.

[7] A. Langseth, J. U. Sørensen and J. R. Nielsen, J. Chem. Phys. 2, 402 (1934).

[8] J. Cabannes and A. Rousset, Ann. de physique 19, 229 (1933).

[9] J. D. Stranathan, Rev. Sci. Inst. 5, 334 (1934).

[10] C. P. Smyth and S. O. Morgan, J. Am. Chem. Soc. 50, 1547 (1923).

outlet between the prisms of an Abbe refractometer. No appreciable loss of solute by evaporation occurred in the time of a measurement. All measurements connected with electric moment estimations were made at 25°C.

The corresponding measurements on dimethyl hydrazine and acetaldazine were carried out in essentially the same way, with greater ease owing to their lower volatility than that of azomethane.

RESULTS

Azomethane

Figure 1 shows the infrared absorption spectrum of azomethane, and the data on the infrared and Raman spectra are collected in Table I. The column headed I gives a rough estimate of relative intensities of Raman bands, and a crude estimate of the relative intensities of the absorption bands can be made from the pressures at which the different bands shown in Fig. 1 were measured.

ρ_n is the depolarization factor of the scattered radiation for unpolarized incident light =

intensity of scattered light whose electric vector vibrates $\parallel$ to direction of incident beam

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intensity of scattered light whose electric vector vibrates $\perp$ to direction of incident beam.

Dielectric constant measurements

In Table II are summarized the measurements and the derived polarizations for azomethane dissolved in n-heptane at 25°C. c is the mole fraction of azomethane, d the density, ϵ the dielectric constant, n_D the refractive index for D, P_{12} the total molar polarization of the solution,

TABLE II. *Dielectric constants and polarizations of azomethane in n-heptane at 25°C.*

c	d_4^{25}	ϵ	n_D	P_{12} cc	P_1 cc	P_1^0 cc
0.1477	0.6841	1.901	1.3819	31.707	15.572	16.249 (15.49)
0.0872	0.6821	1.909	1.3839	32.864	15.642	16.378 (15.63)
0.0619	0.6810	1.912	1.3849	33.358	16.010	16.769 (16.02)
					Mean 15.74	15.72

P_1 the total polarization of azomethane in solution and P_1^0 the electronic polarization of azomethane in solution, calculated from refractive indices for D. Under each value of P_1^0 is a bracketed figure 5 percent less, which is taken to be the value of the electronic polarization for a static field. The measured values of the relevant constants for n-heptane required in the computation of P_1 and P_1^0 were, $\epsilon = 1.920$, $d = 0.6794$, $n_D = 1.3867$, yielding P_2, the total molar polarization of heptane, equal to 34.50 cc.

It is immediately clear that there is no excess in the total molar polarization of azomethane in these solutions over the electronic contribution, indicating the absence of a permanent electric moment in azomethane under these conditions.

N — N′ dimethylhydrazine and acetaldazine

Table III summarizes the Raman spectra of these compounds, and Table IV the dielectric measurements. In these cases the electronic polarization, P_1^0, has been calculated from the refractive indices and densities of the pure substances, a procedure justified by the well-known independence, to a first approximation, of this quantity on the state of aggregation of the substance. The relevant data are, for the hydrazine, $n_D = 1.4194$, $d_4^{25} = 0.8270$, and for acetaldazine, $n_D = 1.4401$, $d_4^{25} = 0.8311$. Incidentally, we have also found the dielectric constant of acetaldazine at 25° to be 4.435 ± 0.005. The total polarizations of the compounds in solution show no distinct trend with concentration, and we have considered it best to take the mean value in calculating the electric moment from the equation $\mu = 0.0127((P_1 - P_1^0)T)^{\frac{1}{2}}$ Debye units. Permanent moments of 1.35 ± 0.15 and $1.16 \pm 0.10\,D$ are found for dimethyl hydrazine and acetaldazine respectively in heptane at 25°C.

DISCUSSION OF RESULTS

Azomethane

We recall again Boersch's elimination of a linear structure for this molecule by electron diffraction experiments, a conclusion consistent with the structure proposed by Brockway and Pauling[11] for methylazide,

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[11] L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. **19**, 860 (1933).

TABLE III. *Raman spectra of $N-N'$ dimethylhydrazine and acetaldazine at 20° C.*

N—N' DIMETHYLHYDRAZINE			ACETALDAZINE		
$\Delta\nu$(cm^{-1})	I	ρ_n	$\Delta\nu$(cm^{-1})	I	ρ_n
473	2	D	374	0	
1010	2		499	5	0.3
1118	2		907	4	D
1201	2		1029	3	D
1301	2		1151	4	D
1465	5		1345	5	D
2790	6	0.25	1389	4	D
2838	4	D	1443	5	.8
2867	4	D	1530	0	
2940	10	.25	1569	2	
2973	9	D	1627	10	.6
3099	3		2866	2	
3226	10	.3	2925	8	.3
3319	6	D	2959	2	
3390	2				

$$N = N - N,$$
$$\diagup$$
$$H_3C$$
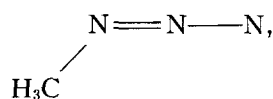
with a C—N—N angle of 135°±15°. On the assumption of lack of free rotation in the nitrogen-nitrogen linkage, we have then the alternatives of distinct *cis* or *trans* forms of azomethane; and the absence of a permanent moment, within our limits of detection, shows immediately and unambiguously that in inert solvents at 25°, the substance is nearly all in the *trans* form. The analogy between azomethane and $p-p'$ dibromazobenzene, from whose zero moment Boersch had already concluded that the *trans* form was the most likely structure for azomethane, is therefore a valid one.

The spectral results are also in accord with a *trans* configuration. The structure

$$CH_3$$
$$\diagup$$
$$N = N$$
$$\diagup$$
$$H_3C$$
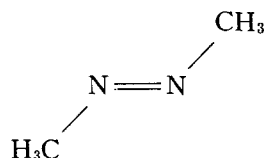
has a center of symmetry, the corresponding *cis* form has not; the former form will have two sets of fundamental frequencies, one of which will be active in Raman scattering only, the other in infrared absorption only; for the *cis* form the excitation of certain modes of vibration by both mechanisms will be possible. In the Raman spectrum of liquid azomethane we have found 12

relatively strong frequencies, half of the total $3n-6=24$ vibrations the molecule may possess; the infrared absorption, exclusive of frequencies greater than 3030 cm^{-1}, as we have observed it in the gas, consists of 10 bands. Not all of these are likely to be fundamentals, e.g., the bands at 2392 cm^{-1} and 2597 cm^{-1}; also, the band whose maximum is at 3030 cm^{-1} and possibly some of the others, are almost certainly unresolved complexes of fundamentals, so we do not know how many fundamentals are active in infrared absorption; but the significant point is that with the pronounced exception of the strong Raman frequency 1442 cm^{-1} and the strong infrared frequency 1430 cm^{-1} there is no coincidence of Raman and absorption frequencies.

The skeleton

$$C$$
$$\diagup$$
$$N - N$$
$$\diagup$$
$$C$$
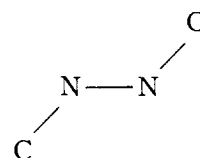
has the symmetry C_{2h}, which will have three modes of vibration symmetrical to the symmetry center, active in scattering, and three antisymmetrical, active in absorption of light.[12] In fact, apart from the frequencies of the hydrogen atoms in the methyl radical, the Raman frequencies of azomethane group themselves into three sets,

TABLE IV. *Polarizations of $N-N'$ dimethylhydrazine and acetaldazine in heptane at 25°C.*

N—N' dimethyl hydrazine					
c	d_4^{25}	ϵ	P_{12} cc	P_1 cc	P_1^0 cc
0.0942	0.6872	2.046	36.245	54.732	17.640
.0523	.6841	1.988	35.495	56.700	"
.0332	.6824	1.951	34.846	50.020	"
.0177	.6810	1.931	34.578	52.350	"
				Mean 55.21	

Acetaldazine					
0.3024	0.7192	2.865	41.422	57.80	26.66
.0953	.6918	2.031	36.449	56.47	"
.0855	.6904	2.026	36.437	56.08	"
.0221	.6822	1.932	34.662	49.57	"
				Mean 54.43	

[12] G. Placzek, *Handbuch der Radiologie*, Vol. VI. 2. p. 293 (Akad. Verlags gesellschaft, Leipzig, 1934).

around the strong frequencies 1442 cm⁻¹, 922 cm⁻¹, and 596 cm⁻¹. These we ascribe to totally symmetrical vibrations of the azomethane molecule; and one other member in each group will be due to a vibration, symmetrical to the symmetry center, in which the phase of one of the hydrogen atoms in each methyl group is opposite to that of the other two. The approximate vibration forms of the carbon-nitrogen skeleton with their proposed frequencies are shown in Fig. 2, in which the motions of the nuclei in ν_4 and ν_6 take place perpendicularly to the molecular plane.

In the vibrational mode ν_1 the two nitrogen nuclei are those which have the greatest amplitude of motion, and in the language of "bond frequencies," we might call this the $N=N$ bond frequency in azomethane and similarly ν_2 the $C-N$ frequency. The value 1442 cm⁻¹ for the $N=N$ frequency in azomethane seems at first sight rather low, in the light of the well-known values of 1620 to 1650 cm⁻¹ for the $C=C$ frequency in ethylenic compounds, and 1710 to 1760 cm⁻¹ for the $C=O$ frequency in aldehydes and ketones. The diatomic N_2 molecule, however, has two excited states, immediately above the lowest state, each with 2 net pairs of bonding electrons, which would be described in the inadequate language of the chemical theory of valence as double bonded.[13]

The lower state, $^3\Sigma_u{}^+$, with the electronic configuration $\sigma_g{}^2\sigma_u{}^2\pi_u{}^3\sigma_g{}^2\pi_g$, has an equilibrium internuclear distance of 1.290A and a frequency of 1460 cm⁻¹ (cf. the Pauling-Huggins $N=N$ distance 1.26A and the other, $^3\Pi_g$, $\sigma_g{}^2\sigma_u{}^2\pi_u{}^4\sigma_g\sigma_u$, an internuclear distance of 1.207A and a frequency of 1733 cm⁻¹. The electronic states immediately above the normal state of the isoelectronic molecule CO are a state K of unknown characteristics and a $^3\Pi$, $\sigma^2\sigma^2\pi^4\sigma\pi$ of internuclear distance 1.205A and frequency 1739 cm⁻¹. The Pauling-Huggins distance for $C=O$ is 1.28A. It seems probable that the state of CO in the carbonyl radical of the aldehydes and ketones can be regarded as derived from the $^3\Pi$ state of CO, and it is evident that the corresponding $N=N$ state in a complex molecule would have a frequency of about 1700 cm⁻¹ and an inter-

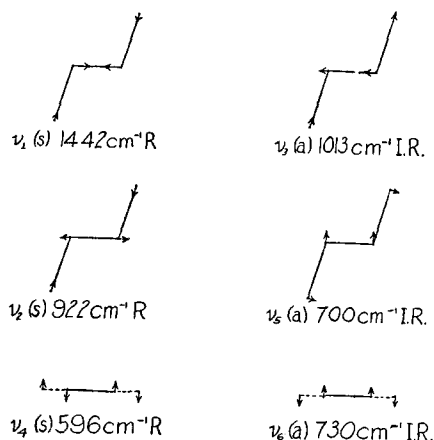¹³ H. Sponer, *Molekulspektren-Tabellen* (Julius Springer, Berlin, 1935), pp. 11 and 32.

FIG. 2.

nuclear distance of somewhat under 1.20A. The observed frequency of 1440 cm⁻¹ and internuclear distance of 1.24A of the $N=N$ bond in azomethane seem reasonably to be derived largely from the $^3\Sigma_u{}^+$ state of the diatomic molecule. Our conclusion therefore is that the Raman frequency 1442 cm⁻¹ in azomethane does represent the $N=N$ vibration frequency, and that this bond is not analogous to the $C=O$ bond, but is one with essentially weaker binding.

The origin of the strong infrared absorption at 1430 cm⁻¹ has still to be discussed. The evidence for the structure proposed for azomethane is very strong, and granting its correctness, according to the selection rules for molecules with symmetry centers, the infrared absorption in question cannot be associated with the $N=N$ vibration. The near coincidence between the absorption and Raman frequency must be accidental. Its obvious origin is in an antisymmetric bending vibration of the H atoms in the methyl groups, which is well known to have a value about 1430 cm⁻¹ and which is a prominent feature of the absorption spectrum of most compounds containing methyl groups; the fairly strong Raman frequency 1376 cm⁻¹ may be the corresponding symmetrical mode.

N·N′ dimethylhydrazine

In the light of Penney and Sutherland's proof of the strong asymmetry of the hydrazine molecule, it is not surprising that dimethylhydrazine likewise shows the characteristics of a strongly asymmetric molecule. In the Raman spectrum
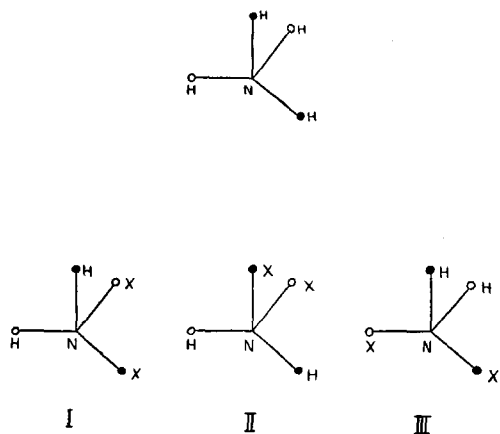
FIG. 3. "End-on" views of hydrazine and the structurally possible N−N disubstituted hydrazines.

there are no strong lines except those corresponding to the C−H and N−H vibrations around 2900 cm^{-1} and 3300 cm^{-1}, respectively, and in particular there is no strong line of about 1000 cm^{-1} in the position to be expected if the two halves of the molecule could exercise a symmetrical vibration with respect to one another. The relatively high value of the electric moment, 1.35 D is practically certain evidence of asymmetry.

We shall assume that the asymmetry in dimethylhydrazine is essentially like that in hydrazine. In the latter molecule, Penney and Sutherland show that, as a result chiefly of the hindrance to free rotation about the N−N bond caused by the interaction of the axially unsymmetrical wave functions of the nitrogen atoms, the most stable arrangement is that in which the bonds radiate from each nitrogen atom at about the tetrahedral angle of 110° and in which the one NH$_2$ group is twisted with respect to the other in such a way that the projections of the NH bonds on one nitrogen atom on a plane perpendicular to the N−N axis have been rotated through 90° with respect to those on the other nitrogen atom.

Three possible structures are now open for a disubstituted hydrazine with the substituents on different nitrogen atoms which are represented in Fig. 3 as I, II and III.

Assuming the valence angles in dimethylhydrazine the same as those given by Penney and Sutherland for hydrazine, and also assuming that the resultant moment of a molecule is

additively compounded of the various "bond moments" present[14] we can compute the moment of the three structures and compare it with experiment. The observed moment of ammonia leads to the value of 1.30 D for the NH bond moment. Assuming now that in the amines the bonds radiate from the nitrogen atom at the tetrahedral angle, as in ammonia, and that in these compounds the negative end of the N−C moment is towards the nitrogen atom, we find from the observed moments of methylamine and trimethylamine, 1.23 and 0.6 D, respectively,[15] that the N−C bond moment is 0.61 D, and that the moment of the group

$$\begin{array}{c} H \\ \diagup \\ N \\ \diagdown \\ CH_3 \end{array}$$
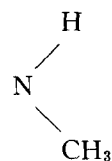
with the same assumption as to valence angles, is 1.28 D at an angle of 28° to the direction of the NH bond in the HNC plane. The N−N link in dimethylhydrazine, assumed to make angles of 110° with the NH and NC bonds, is found to make the angle 122° with the NH·CH$_3$ moments. To calculate the moment of the different structural modifications of dimethylhydrazine, one compounds the 2 moments of magnitude of 1.22 D, each at 122° to the N−N bond, and oriented with respect to each other in the different ways required by the three models. In this way structures I, II, and III are found to have moments of 1.47, 0.54 and 2.00 D, respectively, to be compared with the observed value of 1.35 ±0.15. Models II and III are definitely excluded as preponderant structures in dimethylhydrazine at room temperature; model I has a moment, which in view of the experimental uncertainty and the approximate nature of the assumptions on valence angles and additivity of bond moments made in the calculations, can be regarded as agreeing with the experimental value. It would be regarding the calculations too seriously to conclude that the somewhat lower experimental value of the moment than that calculated for structure I indicated the presence in dimethylhydrazine of a little of structure II; but what

[14] A. Eucken and L. Meyer, Physik. Zeits. 30, 400 (1929).
[15] Trans. Faraday Soc. 30, Appendix to general discussion on dipole moments, pp. lix, lx (1934).

seems certain is that dimethylhydrazine in heptane solution at 25°C is predominately of structure I.

Little can be added at present concerning the Raman spectrum of dimethylhydrazine to the general description already given. Two lines of 1010 cm⁻¹ and 1118 cm⁻¹ seem to be comparable with the pair at 904 cm⁻¹ and 1117 cm⁻¹ of hydrazine in aqueous solution,[16] of which one or other, or both, are due essentially to the $N-N$ vibration, while the line at 473 cm⁻¹ is probably due to the corresponding bending vibration. With respect to acetaldazine we wish at present only to emphasize the asymmetry in the structure indicated by the moment of 1.16 D and the identification of the strongest line in the Raman spectrum, corresponding to a frequency of 1627 cm⁻¹ as the $C : N$ vibration.

SUMMARY

The Raman spectra and electric moments of azomethane, $N-N'$ dimethylhydrazine and acetaldazine, and the infrared absorption of azomethane from 1–15μ are reported. The results indicate a *trans* configuration for azomethane, and an unsymmetrical structure for dimethylhydrazine, derived from Penney and Sutherland's structure for hydrazine. Some of the data are; electric moments, azomethane, O, $N-N'$ dimethylhydrazine, 1.35 D, acetaldazine, 1.10 D; $N=N$ vibration frequency in azomethane 1442 cm⁻¹, $C=N$ vibration frequency in acetaldazine, 1627 cm⁻¹, dielectric constant of acetaldazine at 25°, 4.435.

[16] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Julius Springer, Berlin, 1931), p. 312.

Raman Spectra of Benzene and Isotope Effect

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A faint line accompanying the strong line in the region of 990 cm⁻¹ is observed in the Raman spectra of benzene, chlorobenzene, bromobenzene, toluene and cyclohexane. The relative intensities of the weak 984 cm⁻¹ line and the strong 992 cm⁻¹ line of benzene are measured to be in the ratio 6 : 100. This together with an approximate theoretical estimate support the suggestion that the weak line is due to molecules in which one of the carbon atoms is an isotope of mass 13. The exceedingly low intensity of the corresponding faint line in cyclohexane seems to point to a nonplanar structure. Similar study on the 944 cm⁻¹ line in C_6D_6 is suggested.

INTRODUCTION

THE Raman and the infrared spectra of benzene have been the subject of many investigations and the normal vibrations of the benzene molecule are well known.[1] Of the many Raman lines, the strong and polarized lines at 992 cm⁻¹ and 3060 cm⁻¹ are known to be the frequencies of the symmetrical pulsating motions of the carbon and the hydrogen rings.[2] The line at 992 cm⁻¹ is accompanied by a very faint

line at 984 cm⁻¹. It has been suggested by Gerlach[3] that this faint line may be due to a molecule in which one of the carbon atoms is replaced by a heavy isotope of mass 13. Attempt to settle this question by means of polarization measurement of the weak line by Grassmann and Weiler[4] has not been conclusive because of the difficulty in obtaining exact values for the degree of depolarization of an extremely weak line in close proximity with a very strong one.

[1] K. W. F. Kohlrausch, Physik. Zeits. 37, 58 (1936).
[2] J. Weiler, Zeits. f. Physik 72, 206 (1931).
[3] W. Gerlach, Münch. Ber. 39, Nr. 1 (1932).
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