InfraRed and Raman Spectra of Polyatomic Molecules VI. Triborine Triamine, B3N3H6

Bryce L. Crawford and John T. Edsall

Additional information on J. Chem. Phys.

Infra-Red and Raman Spectra of Polyatomic Molecules

VI. Triborine Triamine, $B_3N_3H_6$*

BRYCE L. CRAWFORD, JR.,** *Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts*
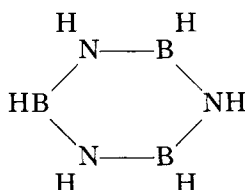
AND

JOHN T. EDSALL, *Department of Physical Chemistry, Harvard Medical School, Boston, Massachusetts*

(Received January 18, 1939)

The Raman spectrum of liquid triborine triamine has been studied, and the infra-red absorption of the gas measured from 2.5 to 24.5μ. The molecule is assumed to be isoelectronic with benzene, belonging to the point group D_{3h}, and an assignment of fundamental frequencies is given, based upon this structure. A normal coördinate treatment has been made, and used to calculate the three inactive frequencies and the isotope shifts due to the B^{10} isotope. The agreement between calculated and observed values is satisfactory except for the nonplanar frequencies, where strong interactions between bonds attached to the aromatic ring in meta-positions are indicated. The fundamental frequencies of triborine triamine are compared with those of benzene; satisfactory correlation is obtained with the benzene frequencies given by Lord and Andrews. The frequencies of the triborine triamine are used together with structural data to calculate the thermodynamic properties of the substance.

TRIBORINE triamine, $B_3N_3H_6$, is one of the most interesting of the boron hydrides. Both chemical evidence and electron-diffraction studies[1] support a structure isoelectronic with benzene, having the configuration:

$$
\begin{array}{ccc}
\text{H} & & \text{H} \\
\text{N}\!\!-\!\!-\!\!\text{B} & & \\
\text{HB} & & \text{NH} \\
\text{N}\!\!-\!\!-\!\!\text{B} & & \\
\text{H} & & \text{H}
\end{array}
$$

The present study was undertaken with a twofold purpose: we wished to study triborine triamine as a molecule containing the B−H and N−H linkages, and we also wished to compare its spectrum with that of benzene.

EXPERIMENTAL

Raman effect

The sample of triborine triamine used was prepared by Dr. Anton B. Burg at the University of Chicago. The material was introduced into a small Pyrex Raman tube (effective volume about 0.3 cc) by distillation *in vacuo*, and the entrance tube sealed off. The spectrum was excited by the blue-violet mercury lines (4047 and 4358A), and photographed with a Hilger E-439 spectrograph. The experimental arrangements, including those used in the polarization studies, have been previously described.[2] The best plates were measured with a comparator, using an argon comparison spectrum, and also microphotometered.

The observed frequencies of all lines found are given in Table I; the measurements are in most cases the averaged results from several plates. A few lines were measured only on the microphotometer tracings; the frequencies given for these lines are enclosed in parentheses. The values for the frequency shifts are collected in Table II, together with the intensity estimates and polarization characters of the lines. A microphotometer tracing of the spectrum is given in Fig. 1.

Polarization studies showed the four most intense lines to be polarized. These lines are marked in Table II, and are shown in the tracings of Fig. 2.

The intense line at 938 cm^{-1}, asymmetrical towards the high frequency side, is a partially

* This material was presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at Milwaukee, September, 1938.
** National Research Fellow in Chemistry.
[1] (a) A. Stock and E. Pohland, Ber. **59B**, 2215 (1926). (b) A. Stock and R. Wierl, Zeits. f. anorg. allgem. Chemie **203**, 228 (1931). (c) A. Stock, *Hydrides of Boron and Silicon* (Cornell University Press, 1933), Chapter XIV. (d) H. I. Schlesinger, L. Horvitz and A. B. Burg, J. Am. Chem. Soc. **58**, 409 (1936). (e) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.* **60**, 1296 (1938). (f) S. H. Bauer, *ibid.* **60**, 524 (1938).
[2] (a) J. T. Edsall, J. Chem. Phys. **4**, 1 (1936). (b) J. T. Edsall and E. B. Wilson, Jr., *ibid.* **6**, 124 (1938).

TABLE I. *Observed Raman frequencies.*

FREQUENCY, CM^{-1}, VAC.	INTENSITY*	ASSIGNMENT**
24181	0	524 k
(23997	0	708 k)
23854	3	851 k
23767	4	938 k
23660	0	856 i
23636	2	1069 k
23571	1	945 i
23477	?	1228 k
23444	0	1072 i
23227	0	$-289\,e$
22793	0?	145 e
22650	3 b	288 e
22470	0?	525 f
22419	3	519 e
22230	0	708 e
22170	4 vb	2535 k
22140	1	798 e
22087	7	851 e
22000	9	938 e
21868	4	1070 e
21568	0	1370 e
21473	0	1465 e
21254	9	3451 k
21095	?	1843 e
21066	2	3450 i
20518	2	2521 g
20410	9 vb	2528 e
(19589	2	3450 g)
(19545	3	3450 f)
(19488	10	3450 e)

* b =broad; vb =very broad.
** The designation of the mercury lines is that of Kohlrausch: e =22938, f =22995, g =23039, i =24516, k =24705 cm^{-1}, *in vacuo.* Frequencies enclosed in parentheses were measured on microphotometer tracings only.

resolved isotopic complex; the calculated shifts are discussed below (Fig. 5).

The lines at 23477 and 21095 cm^{-1} appeared very faintly on one plate only. Their reality is therefore doubtful, and in any case they are extremely weak shifts.

The Raman shift at 145 cm^{-1} is also of very doubtful reality. It is certainly a very weak line at best; moreover, it appeared almost at the edge

of the dark background around the 4358A line. Since the small volume of material necessitated rather long exposures, this background was quite intense, making it very difficult to decide as to the reality of the 145 cm^{-1} line. Observations near the 4047A line were of no help, because of the weaker excitation and also because of the proximity of the 4078A line. The examination of plates taken with benzene in the Raman tube also failed to give a decisive answer.

Infra-red absorption

The infra-red spectrometer has been previously described.[3] The absorption was measured from 2.5 to 24.5μ, using rocksalt and KBr prisms in the appropriate regions of the spectrum. The cells used, 30 cm in length, were closed with KBr windows. The pressure of the triborine triamine was controlled by maintaining a bath around a small side-tube attached to the cell, the temperature of the bath being adjusted to give the vapor pressure desired.

The absorption curve is shown in Fig. 3. The frequencies of the absorption maxima are listed in Table III.

Certain of the bands require some comment. The reality of the shoulder at 480 cm^{-1}, and of the very weak band at 570 cm^{-1}, is somewhat doubtful; unfortunately we could not obtain pressures higher than 100 mm, which might have brought out these bands more definitely. The frequency 415 cm^{-1}, given for the lowest lying band, may be in error. This frequency lies near the long wave-length limit of our instrument, using the KBr prism; the effects of stray radia-

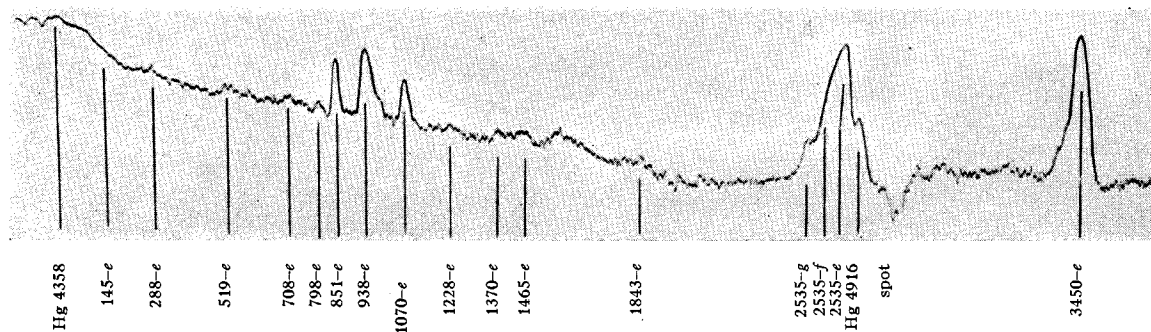[3] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).

FIG. 1. Microphotometer tracing of the Raman spectrum of triborine triamine, excited by the Hg 4358A line.
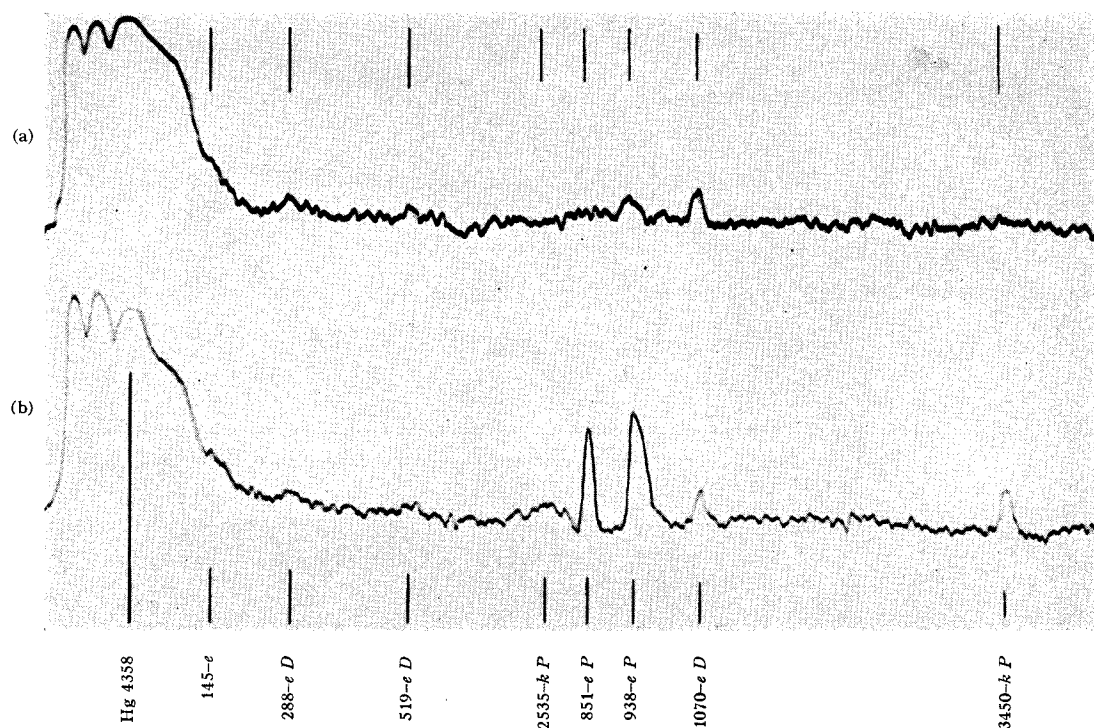
FIG. 2. Microphotometer tracings of the Raman spectrum of triborine triamine, excited by plane polarized light oriented (a) parallel and (b) perpendicular to the optical axis of the Raman tube. Polarized lines are marked P, depolarized lines, D.

tion become of greatly increased importance in this region, and may operate to shift the apparent absorption maximum of this band. The presence of a fairly strong absorption band at approximately 415 cm^{-1}, however, cannot be doubted.

The frequencies of the bands lying above 2000 cm^{-1} could not be determined as accurately as the lower frequencies, since the dispersion of rocksalt in this spectral region is quite low.

NORMAL MODES OF VIBRATION

Symmetry

Triborine triamine, isoelectronic with benzene, may be assigned to the point-group D_{3h}; the reduced representation for the internal vibrations then has the structure:[4]

$$\Gamma = 4A_1' + 3A_2' + 3A_2'' + 7E' + 3E'';$$

i.e., there are 20 distinct frequencies of which 10 are doubly degenerate; of these 20, 14 are planar vibrations and six involve motions perpendicular

to the plane. This is entirely similar to the case of benzene, which has been treated by Wilson;[5] the similarity and the relations between the frequencies of the two molecules are shown in Table IV.

This table also gives the selection rules for the two molecules. It will be seen that those for

TABLE II. Raman shifts, polarizations and assignments.

FREQUENCY, CM^{-1}, VAC.	INTENSITY, POLARIZATION*	ASSIGNMENT	SYMMETRY
145	0?	—	—
288	2 b	Fund.	E''
519	3 D	Fund.	E'
708	1	Fund	E'
798	2	Fund.	E''
851	6 P	Fund.	A_1'
938	7 P	Fund.	A_1'
1070	5 D	Fund.	E''
1228	?	938+288 = 1226	E''
1370	1	525+850 = 1375	E'
1465	1	Fund.	E'
1843	?	917+938 = 1855	E'
2535	9 vb P	Fund.	A_1'
3450	10 P	Fund.	A_1'

* b = broad, vb = very broad, P = polarized, D = depolarized.

---

[4] J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. 8, 317 (1936).

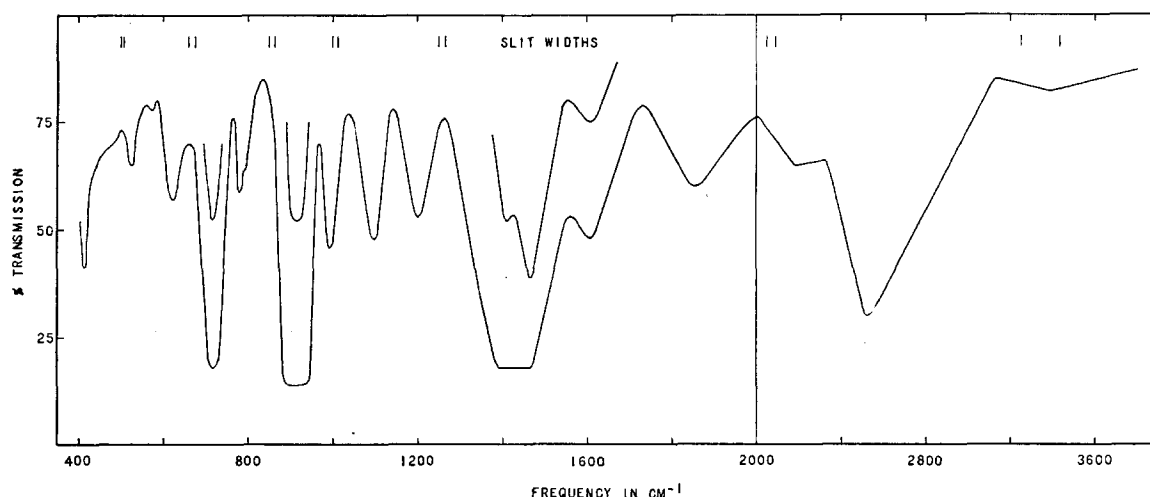[5] E. B. Wilson, Jr., Phys. Rev. 45, 706 (1934).

FIG. 3. Infra-red absorption of triborine triamine. Path length, 30 cm; pressures of 100 and 10 mm.

triborine triamine are unusually favorable for analysis, as they distinguish unambiguously between the various symmetry classes. The rules also allow all but three of the $B_3N_3H_6$ fundamentals to be directly observed, while only nine benzene fundamentals are observable.

Normal coördinate treatment

A normal coördinate treatment was carried out not only to investigate the magnitudes of the force constants in this molecule, but also to serve as a guide in the assignment of the fundamentals, and to enable calculation of the three completely inactive frequencies belonging to the class A_2'.

TABLE III. *Infra-red absorption bands and assignments.*

FREQUENCY, CM⁻¹	INTENSITY	ASSIGNMENT	SYMMETRY
415	40	Fund.	A_2''
480	?	——	——
525	20	Fund.	E'
570	5	$288^2 = 576$	$A_1' + E'$
622	30	Fund.	A_2''
717	70	Fund.	E'
778	30	$1070 - 288 = 782$	$A_1' + A_2' + E'$
790	5	$1098 - 288 = 810$	E'
917	100	Fund.	E'
990	40	$717 + 288 = 1005$	$A_1'' + A_2'' + E''$
1098	40	Fund.	A_2''
1199	35	$917 + 288 = 1205$	$A_1'' + A_2'' + E''$
1410	30	$717^2 = 1434$	$A_1' + E'$
1466	85	Fund.	E'
1610	30	Fund.	E'
1850	30	$917 + 938 = 1855$	E'
2174	10	$1466 + 717 = 2183$	$A_1' + A_2' + E'$
2519	60	Fund.	E'
3400	5	Fund.	E'

A simple valence-force potential function, without interaction constants,[6] was used; it was based on that proposed by Wilson[5] for benzene. Because of the greater number of bond types in triborine triamine, nine force constants were required to correspond to the six used for benzene.

The potential function for planar distortions is:

$$2V = K\Sigma_6(\Delta R_i)^2 + q_B\Sigma_3(\Delta r_i)^2 + q_N\Sigma_3(\Delta s_i)^2$$
$$+ kR_0^2\Sigma_6(\Delta\alpha_i)^2 + H_Br_0^2\Sigma_3(\Delta\beta_i)^2 + H_Ns_0^2\Sigma_3(\Delta\gamma_i)^2.$$

Here R_i, r_i, s_i are the lengths of the ith B−N, B−H and N−H bonds, respectively, and R_0, r_0, s_0 are the equilibrium bond lengths. α_i is the ith B−N−B or N−B−N angle ($\alpha_0 = 120°$). $\Delta\beta_i$ measures the deviation of the ith B−H bond from the bisector of the N−B−N angle; $\Delta\gamma_i$ is the corresponding angle for the N−H bond ($\beta_0 = \gamma_0 = 0$). K, q_B, q_N, k, H_B and H_N are the appropriate force constants.

For nonplanar distortions:

$$2V = h_Br_0^2\Sigma_3(\Delta\lambda_i)^2 + h_Ns_0^2\Sigma_3(\Delta\mu_i)^2 + \kappa d^2\Sigma_6(\varphi_i)^2.$$

Here $\Delta\lambda_i$ measures the deviation of the ith B−H bond from the plane of the adjacent B−N bonds, and $\Delta\mu_i$ is the corresponding N−H bond angle. φ_i is the angle of twist of the ith B−N

---

[6] Corrections to allow for the effect of hydrogen-hydrogen repulsion on the force constants H_N and H_B, analogous to those used by Lord and Andrews (reference 12) in their treatment of benzene, were not made. Recent evidence on hindered rotation of methyl groups seems to indicate that other types of interaction are more important than that calculated from present theory; we therefore considered it advisable to omit interaction forces altogether.

TABLE IV. *Symmetry classes of the normal vibrations of* $B_3N_3H_6$ *and* C_6H_6.*

$B_3N_3H_6(D_{3h})$		$C_6H_6(D_{6h})$	
PLANAR:			
$4 A_1'$	(R, P)	$2 A_{1g}$	(R, P)
		$2 B_{1u}$	(In)
$3 A_2'$	(In)	A_{2g}	(In)
		$2 B_{2u}$	(In)
$7 E'$	$(R, D; IR)$	$4 E_{2g}$	(R, D)
		$3 E_{1u}$	(IR)
NONPLANAR:			
$3 A_2''$	(IR)	$2 B_{2g}$	(In)
		A_{2u}	(IR)
$3 E''$	(R, D)	$2 E_{2u}$	(In)
		E_{1g}	(R, D)

* R, P = Raman active, polarized $(\rho \leqq 6/7)$; R, D = Raman active, depolarized $(\rho = 6/7)$; IR = Infra-red active; In = Inactive.

bond, and d is the projection of the equilibrium B−N distance on a line perpendicular to the adjacent B−N bond $(d = R_0 \cos 30°)$. h_B, h_N and κ are the appropriate force constants; κ arises from the partially double-bond character of the B−N bond, similar to that of the isoelectronic C−C bond in benzene.

S_1 : BH units S_2 : NH units

S_3 : B - H S_4 : N - H
$m_B/m_H = 11$ $m_N/m_H = 14$
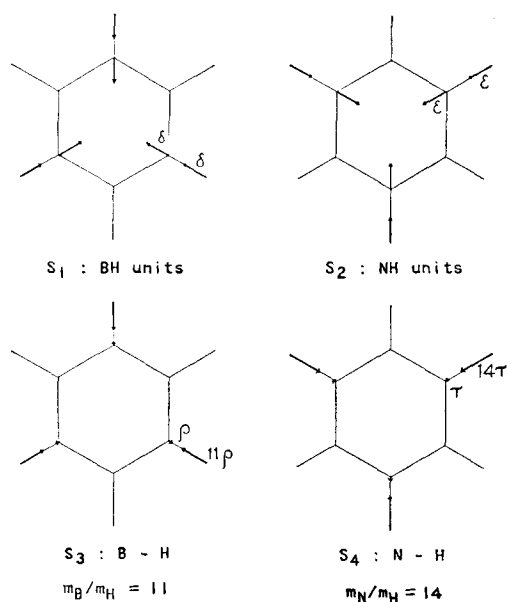
FIG. 4. Symmetry coördinates for the A_1' factor of the secular equation.

Approximate factoring

Using the experimentally justified concept of "bond frequencies" which remain approximately constant in different molecules, we may characterize the modes of vibration belonging to the various symmetry classes as shown in Table V.

The B−H and N−H stretching frequencies will lie much higher than the other frequencies of the molecule, and will interact with them to only a slight extent. In treating the A_1' and E'

TABLE V. *Types of vibrations in triborine triamine. The force constants involved in each symmetry factor are given in parentheses.*

PLANAR: A_1' (R, P)	A_2' (In)	E' $(R, D; IR)$
(K, k, q_B, q_N) N−H stretching B−H stretching ring distortion ring distortion	(K, H_B, H_N) N−H bending B−H bending ring distortion	$(K, k, H_B, H_N, q_B, q_N)$ N−H stretching B−H stretching N−H bending B−H bending ring distortion ring distortion ring distortion

NONPLANAR: A_2'' (IR)	E'' (R, D)
(κ, h_B, h_N) N−H bending B−H bending ring distortion	(κ, h_B, h_N) N−H bending B−H bending ring distortion

factors of the secular equation, we may choose symmetry coördinates such that one will involve B−H stretching, one N−H stretching, and the rest involve motions in which the BH and NH groups move as units. Such symmetry coördinates for the A_1' factor are shown in Fig. 4. It is then found that the interaction terms between the symmetry coördinates involving high frequency stretchings and the other coördinates of the same symmetry factor are comparatively small, and may be neglected in the first approximation. In the final treatment, perturbation methods may be applied;[7] the correction terms are small. This method of approximate factoring was useful in treating the A_1' and E' factors; it was indeed invaluable in the latter case, which was effectively reduced from an equation of the seventh order to a more manageable quintic.

[7] J. H. Van Vleck, Phys. Rev. **33**, 484 (1929); O. M. Jordahl, *ibid.* **45**, 87 (1934); E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. **4**, 260 (1936). We are indebted to Professor Wilson for suggesting the use of this type of symmetry coördinate and the application of the perturbation treatment to the resulting secular equation.

The frequency expressions which were obtained are too complicated to be reproduced here. The force constants involved in each of the symmetry factors are shown in Table V.

THE VIBRATION FREQUENCIES

The totally symmetric vibrations

In spite of the favorable way in which the selection rules discriminate between the various symmetry classes, a complete assignment cannot be made on this basis alone. In the first place, some of the E' frequencies, which should appear in both Raman and infra-red, are apparently too weak in the Raman effect to be detected; i.e., there are too few coincidences between Raman and infra-red. Moreover, certain combination frequencies appear with intensities comparable to those of the fundamentals.

For the totally symmetric frequencies (A_1'), there is no ambiguity. The four intense Raman lines with shifts of 851, 938, 2535 and 3450 cm^{-1} are all polarized, and are the only lines found to be polarized; they may therefore be assigned at once to the A_1' class.

The frequencies at 3450 and 2535 cm^{-1} obviously belong to the N$-$H and B$-$H stretchings, respectively. The N$-$H frequency lies somewhat above the values found for amines, which range around 3350 cm^{-1}; this is perhaps similar to the higher frequency of the C$-$H vibration in benzene, compared to the C$-$H frequencies in methyl groups. The B$-$H frequency of 2535 cm^{-1} may be compared with the Raman line recently found in B$_2$H$_6$ by Anderson and Burg,[8] at 2523 cm^{-1}. The assignment proposed by these authors postulates a resonance splitting which gives this line and one at 2102 cm^{-1}; on this basis, the true B$-$H fundamental in B$_2$H$_6$ would lie considerably lower than that in triborine triamine. The diatomic molecule BH has, in the ground state $(A^1\Sigma^+)$, $\omega_e = 2230$ cm^{-1}; in the $C^1\Pi$ excited state, $\omega_e = 2450$ cm^{-1}.[9]

The assignment of these four lines permitted the evaluation of the constants K, k, q_B and q_N (see Tables VI and VII); these constants were used in the E' and A_2' factors also.

[8] T. F. Anderson and A. B. Burg, J. Chem. Phys. 6, 586 (1938).
[9] H. Sponer, *Molekulspektren* (Berlin, 1935), pp. 24-25.

The B^{10} isotope effect

The vibration of frequency 938 cm^{-1} involves relatively large motions of the BH groups, and is therefore sensitive to changes in the mass of the boron atom. The B^{10}/B^{11} ratio is about $\frac{1}{4}$; hence the relative abundance ratios for the four molecules B$_3^{11}$N$_3$H$_6$, B^{10}B$_2^{11}$N$_3$H$_6$, B$_2^{10}$B^{11}N$_3$H$_6$, B$_3^{10}$N$_3$H$_6$, on a random chance basis, are

TABLE VI. *The fundamental frequencies, calculated and observed, of triborine triamine and of benzene, in* cm^{-1}.

SYM-METRY	B$_3$N$_3$H$_6$ FREQUENCY OB-SERVED	CALC'D	C$_6$H$_6$ FREQUENCY OB-SERVED	CALC'D (L AND A)†	ASSIGNED (ING.)**	SYM-METRY
A_1'	851	845	992	993	(992)	A_{1g}
	938	940	—	1008	766	B_{1u}
	2535	2544	3061	3061	(3061)	A_{1g}
	3450	3463	—	3063	3062	B_{1u}
E'	525	537	606	608	(606)	E_{2g}
	717	745	1037	1030	(1037)	E_{1u}
	917	954	1178	1170	(1178)	E_{2g}
	1466	1320	1485	1480	(1485)	E_{1u}
	1610	1593	1596	1645	(1596)	E_{2g}
	2519	2544	3047	3107	(3047)	E_{2g}
	3400	3463	3080	3080	(3080)	E_{1u}
A_2'	—	800	—	1145	1145	B_{2u}
	—	1110	—	1190	1240	A_{2g}
	—	1650	—	1854	1720	B_{2u}
E''	288	283	(406)*	406	(low)	E_{2u}
	798	790	850	850	(849)	E_{1g}
	1070	1086	—	1160	890	E_{2u}
A_2''	415	403	—	538	(low)	B_{2g}
	622	756	671	783	(671)	A_{2u}
	1098	1278	—	1520	1000	B_{2g}

* Lord and Andrews' assignment, assuming that intermolecular forces in the liquid break down the selection rules and allow this forbidden line to appear.
** Reference 9; frequencies in parentheses are those observed; others are from combination assignments and reduced mass calculations.
† Reference 10; frequencies calculated from Wilson's equations.

TABLE VII. *Force constants for triborine triamine and for benzene.**

B$_3$N$_3$H$_6$ CONSTANT	VALUE (10^5 DYNE/CM)	C$_6$H$_6$ CONSTANT	VALUE (10^5 DYNE/CM)
Planar			
K (B$-$N stretching)	6.300	K (C$-$C stretching)	7.58
k (B$-$N$-$B or N$-$B$-$N bending)	0.525	k (C$-$C$-$C bending)	0.65
H_B (B$-$H bending)	0.35	H (C$-$H bending)	0.76
H_N (N$-$H bending)	0.65		
q_B (B$-$H stretching)	3.423	q (C$-$H stretching)	5.05
q_N (N$-$H stretching)	6.524		
Nonplanar			
κ (B$-$N torsion)	0.10	κ (C$-$C torsion)	0.23
h_B (B$-$H bending)	0.23	h (C$-$H bending)	0.34
h_N (N$-$H bending)	0.42		

* Constants for benzene from Lord and Andrews, reference 6.

50 : 40 : 10 : 1. The isotopic shifts are 15, 27, and 38 cm^{-1}.[10] The comparison given in Fig. 5 justified the assignment of the high frequency satellites of the 938 cm^{-1} Raman line to the various isotopic molecules involving B^{10}; the isotopic lines were not completely resolved with our instrument.

The E' and A_2' vibrations

The frequencies of the E' class should appear in both infra-red and Raman effect. The infra-red bands at 2519 and 3400 cm^{-1} are obviously to be assigned to the E' B$-$H and N$-$H stretchings (see Table V). These frequencies are either too weakly Raman active to appear, or they are overlaid by the more intense lines of the A_1' fundamentals. (The discrepancy in the frequencies is within the rather large error of the infra-red values in this region of the spectrum.)

There are three obvious coincidences at 525, 717 and 1466 cm^{-1}; these may also be assigned to E' vibrations. Their intensities mark them as fundamentals. There is also an apparent coinci-

---

[10] The isotopic shifts are easily calculated by regarding the change of mass as a perturbation in the kinetic energy, and writing the secular equation for the isotopic molecule in terms of the normal coördinates of the "unperturbed" molecule. The secular equation for the "perturbed" frequencies, λ, is

$$\left| \lambda_k^0 \delta_{kl} - \lambda[\delta_{kl} + \sum_i \Delta m_i (l_{ik} \cdot l_{il})] \right| = 0.$$

Here the subscripts k and l refer to normal modes of vibration which are of approximately the same frequency and are in the same symmetry class of the *isotopic* molecule. λ_k^0 is the frequency parameter $(\lambda_k^0 = 4\pi^2 c^2 \omega_k^2)$ for the kth mode of the unperturbed molecule; Δm_i is the change of mass of the ith atom; l_{ik} is the *vector* displacement of the ith atom in the kth mode, normalized to

$$\sum_i m_i l_{ik}^2 = 1$$

and δ_{kl} is the Kronecker symbol. In the cases B^{10}B$^{11}_2$N$_3$H$_6$ and B$^{10}_2$B^{11}N$_3$H$_6$, molecules of symmetry C_{2v}, the 917 cm^{-1} frequency (E' of D_{3h} in B$^{11}_3$N$_3$H$_6$) and the 938 cm^{-1} frequency belong to the same symmetry class, A_1 of C_{2v}; hence these two modes must be considered and the secular equation for the isotopic frequency is a quadratic. In the B$^{10}_3$N$_3$H$_6$ case, the isotopic molecule also has the symmetry D_{3h}, and only the 938 cm^{-1} frequency need be considered. The secular equation reduces to

$$\lambda_k^0 - \lambda(1 + \sum_i \Delta m_i l_{ik}^2) = 0$$

or, changing over to frequencies instead of the parameters λ,

$$\frac{d\nu}{\nu} = -(\tfrac{1}{2})\sum_i \Delta m_i l_{ik}^2.$$

This last result has been given by E. Teller (*Hand- und Jahrbuch der chemischen Physik* (Leipzig, 1934), Vol. 9, p. 142 *et seq.*). We are indebted to Professor Wilson for the results given above.
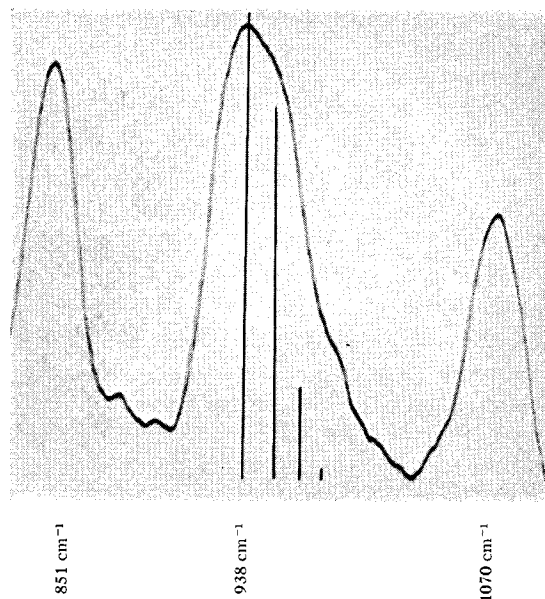

FIG. 5. Enlarged microphotometer tracing of the 938 cm^{-1} Raman line, compared with the components calculated for isotopic molecules. Heights of the calculated lines correspond to the relative intensities to be expected.

---

dence between the Raman frequency of 798 and the infra-red frequency of 790 cm^{-1}. Here, however, the infra-red band is so extremely weak, being indeed a mere shoulder on the rather weak 778 cm^{-1} band, that it cannot reasonably be assigned to a fundamental. It seems more probable that the fairly intense Raman line is due to a fundamental active only in the Raman effect, while the infra-red shoulder is to be assigned to some combination tone. There may also be some question of coincidence between the Raman line at 1070 cm^{-1} and the infra-red band at 1098 cm^{-1}; the discrepancy of 28 cm^{-1} seems rather large, however, and we have preferred to assign these frequencies to separate vibrations.

There are still two E' frequencies to be assigned. The very strong infra-red band at 917 cm^{-1} is surely a fundamental, and may satisfactorily be assigned to this class; it will appear below that the only alternative assignment, to the A_2'' class, is quite unsatisfactory.

To fix the remaining E' frequency, we may use the constants already determined, K, k, q_B and q_N, in the E' factor of the secular equation; these serve to fix one E' frequency at about 1600 cm^{-1}, for any possible values of H_B and H_N. We there-

fore assign the infra-red band at 1610 cm^{-1} to this frequency.

The new constants H_B and H_N were fitted to the 717 and 917 cm^{-1} frequencies. The agreement between calculated and observed values for the E' fundamentals (Table VI) is quite satisfactory except for the 1466 cm^{-1} frequency. Here the error amounts to ten percent; such agreement is perhaps all one has a right to expect when interaction terms are completely neglected.

The constants K, H_B and H_N were used to calculate the inactive planar frequencies (A_2') as given in Table VI. While these values are not as reliable as one might wish, they are sufficiently accurate for many purposes, such as the calculation of thermodynamic properties.

The nonplanar vibrations

Turning to the E'' class, which should give depolarized Raman lines, we assign the 798 cm^{-1} line, discussed above, to this class. The 288 and 1070 cm^{-1} lines obviously belong to the E'' group, and the assignment is thus completed. From these three frequencies the constants κ, h_B and h_N were determined.

The frequencies of the A_2'' vibrations were then calculated to be 403, 756 and 1278 cm^{-1}. The infra-red band at 415 cm^{-1} may at once be assigned to the low frequency A_2'' vibration. We assigned the 1098 cm^{-1} band to the high frequency N$-$H bending vibration, being led to this choice by the fact that we could find no other really satisfactory assignment for this band; other possible choices for the A_2'' fundamental (the 1199 and 1410 cm^{-1} bands) could be assigned as combination tones. The large discrepancy between the calculated and observed values will be discussed below.

For the B$-$H bending vibration, of calculated frequency 756 cm^{-1}, we may consider the bands at 622 and 778 cm^{-1}; it seems unlikely that the frequency could lie near 717 cm^{-1} and be so completely masked by the E' fundamental that no asymmetry of the band would result. Since the N$-$H bending frequency was found to lie considerably below the calculated value, it may reasonably be supposed that a similar discrepancy would exist in the case of the B$-$H bending frequency; we therefore chose the 622 cm^{-1} band for this assignment. This choice receives a *posteriori* support from the close analogy between the out-of-plane B$-$H, N$-$H and C$-$H bending frequencies, which appears when we compare the benzene spectrum with that of triborine triamine.

The calculated and observed fundamentals are collected in Table VI; the force constants are in Table VII. The assignments of all the observed frequencies are given in Tables II and III. Satisfactory assignments were found for all the observed frequencies except the Raman line at 145 cm^{-1} and the infra-red band at 480 cm^{-1}; both these frequencies are extremely doubtful, and are in fact included merely for the sake of completeness.

It cannot be claimed that all alternative assignments have been rigorously excluded in the above argument. However, in exploring the various alternatives, we have been unable to find any other assignment which was at all acceptable, unless we postulated that the higher E'' frequencies do not appear. While this possibility cannot be rejected, it would make a complete assignment impossible, and the assignment given above is in any case more reasonable and satisfactory than the alternatives.

COMPARISON WITH BENZENE

Assignments of all the fundamental frequencies of benzene, both observable and inactive, have been made by Ingold and his co-workers[11] and by Lord and Andrews.[12] The two sets of assigned fundamentals, which agree quite closely, are compared with the corresponding fundamentals of triborine triamine in Table VI. The force constants are compared in Table VII.

Figure 6 shows graphically the comparison given in Table VI. The correlation between the two spectra is, on the whole, quite pleasing. The correspondence of the N$-$H and B$-$H stretching frequencies needs no comment.

With respect to the lower frequencies, involving bending vibrations and ring distortions, in almost all the cases in which both the benzene and the $B_3N_3H_6$ frequencies are observed, the benzene frequency is the higher.[13] The benzene

[11] C. K. Ingold *et al.*, J. Chem. Soc. 912 (1936).
[12] R. C. Lord, Jr., and D. H. Andrews, J. Phys. Chem. 41, 149 (1937).
[13] The single exception occurs in the E' class, where the $B_3N_3H_6$ frequency at 1610 is slightly higher than that of C_6H_6 at 1596 cm^{-1}. This may be looked upon as a case of
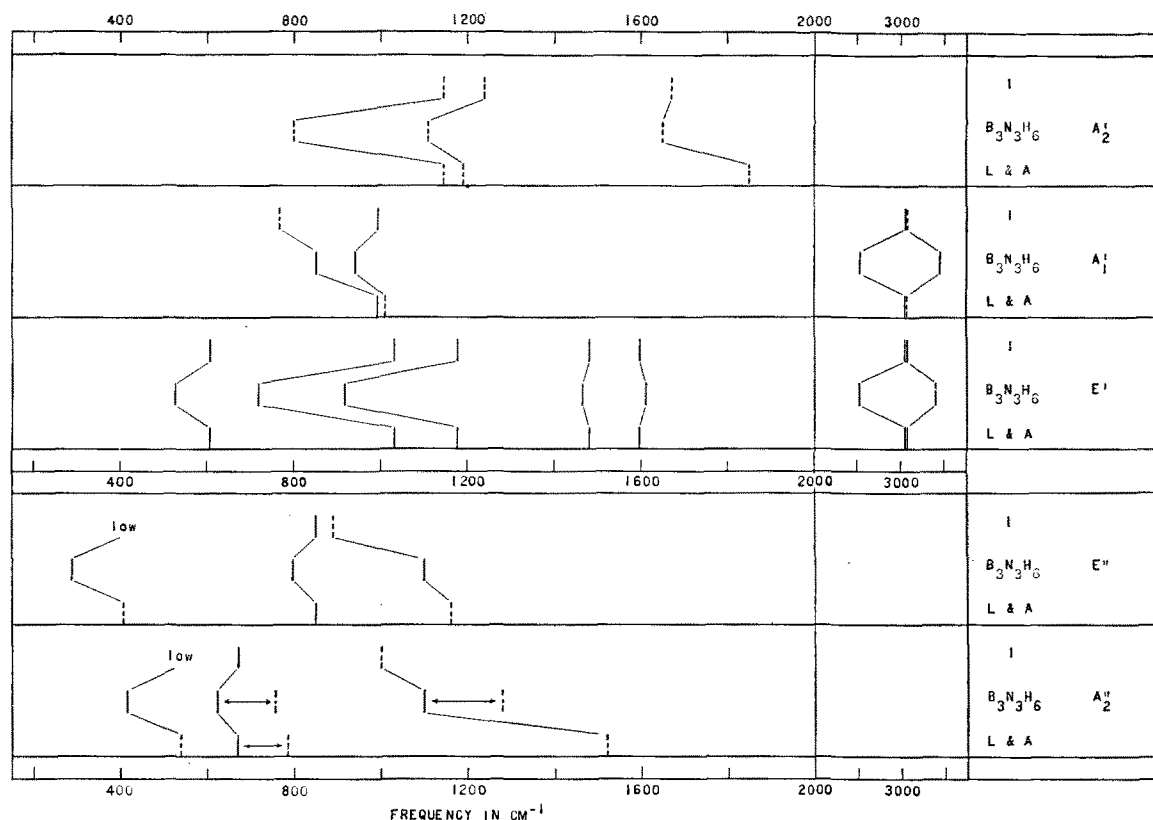
FIG. 6. Comparison of the fundamental frequencies of triborine triamine and benzene. Observed frequencies are represented by solid lines, calculated frequencies by broken lines. In each symmetry class of $B_3N_3H_6$, the benzene fundamentals proposed by Ingold and co-workers are plotted above the corresponding frequencies of $B_3N_3H_6$, and those proposed by Lord and Andrews below; corresponding fundamentals are connected. In the A_2'' class, it will be noted that both observed and calculated values are plotted for two $B_3N_3H_6$ and one C_6H_6 fundamentals.

values calculated by Lord and Andrews also lie above the corresponding observed $B_3N_3H_6$ values, while those given by Ingold and his collaborators are lower in three instances (A_1', 766; E'', 890; A_2'', 1000). From the instances in which the frequencies of both molecules are observed, it would seem reasonable to suppose that the benzene frequencies would lie higher in all cases; from this viewpoint, the $B_3N_3H_6$ spectrum offers indirect evidence in favor of Lord and Andrews' set of benzene fundamentals rather than those of Ingold and his co-workers.

The correlation between the lowest nonplanar frequencies of the two molecules (A_2'' and E'') is

classical resonance; the benzene fundamentals at 1485 and 1596 cm^{-1} are in different symmetry classes and cannot interact, while in $B_3N_3H_6$ the corresponding vibrations can interact to cause a slight spreading of the frequencies, observed at 1466 and 1610 cm^{-1}. It should also be remembered that the value 1596 cm^{-1} (C_6H_6) is the mean of a quantum-mechanical resonance doublet, and may itself be somewhat in error.

quite satisfactory, and supports Lord and Andrews' assignment of the weak 406 cm^{-1} Raman line in liquid benzene to the forbidden E_{2u} fundamental.

The nonplanar bending frequencies of the C$-$H bond in benzene and of the B$-$H and N$-$H bonds in triborine triamine present a curious parallelism. For each type of bond, this bending is involved in fairly pure form in a pair of vibrations of which one is infra-red, the other Raman active; thus in benzene the 850 and 671 cm^{-1} frequencies involve the C$-$H bond, and in triborine triamine the 798 and 622 cm^{-1} frequencies involve the B$-$H bond and the 1070 and 1098 cm^{-1} frequencies, the N$-$H bond. In each case, the infra-red active vibration bends opposite bonds in the *same* direction, while the Raman active vibration bends opposite bonds in *opposite* directions. Thus in benzene, in the infra-red active motion the carbon ring oscillates

against the hydrogen ring along the sixfold axis; in the Raman active motion, the two rings rock against each other, rocking about one of the twofold axes. (See numbers 11 and 10a in Fig. 3 of reference 5.) The potential functions used for the two molecules neglect possible interactions between opposite bendings. With this assumption, the force constant (e.g., h_B) was fitted to the Raman frequency (798 cm^{-1}) and then used to calculate the value of the infra-red frequency (756 cm^{-1}). The discrepancies between these calculated values and the observed infra-red frequencies amount to 16, 18 and 14 percent for the C—H, B—H and N—H vibrations, respectively.

These large discrepancies indicate quite strong interactions between opposite bonds attached to an aromatic ring. Moreover, while the benzene discrepancy could be accounted for by postulating such interaction between bonds attached in the *para* positions, the discrepancies in triborine triamine make it necessary to assume interactions between bonds attached in the *meta* positions. It is unfortunate that the inactive character of the A_2' vibrations precludes investigation of the possible meta-position interactions in the planar bending vibrations.

THERMODYNAMIC PROPERTIES

The entropy, free energy function, and heat capacity for triborine triamine (perfect gas at 1 atmos. pressure) were calculated at several temperatures by standard statistical methods.[14] In calculating the translational and rotational contributions, the following values were used: atomic weights, 10.82, 14.008, 1.008 for B, N and H, respectively; symmetry number, 6; bond angles (B—N—B, B—N—H, etc.), 120°; interatomic distances,[1f] B—N, 1.44, B—H, 1.20, N—H, 1.02A. The entropy due to nuclear spin was neglected, in accordance with the usual convention of "virtual" entropy. In calculating the vibrational contributions, the observed fundamental frequencies as listed in Table VI were used for all but the three inactive fundamentals; the calculated values for these frequencies were used of necessity. The results of the calculations are given in Table VIII.

[14] L. S. Kassel, Chem. Rev. **18**, 277 (1936).

TABLE VIII. *Thermodynamic properties of triborine triamine, calculated for the perfect gas at 1 atmos. pressure, in cal./mole/degree. Values of the universal constants were taken from the Int. Crit. Tab.*

T, °K	S^0	$-(F^0-E_0^0)/T$	C_p^0
298.1	73.7	60.4	23.3
326 (b.p.)	75.8	61.5	25.3
350	77.7	62.6	27.1
400	81.5	64.8	30.4
500	88.9	68.7	36.0
600	95.9	72.6	40.5
700	102.5	76.6	44.2
800	108.5	80.2	47.2
900	114.2	83.6	49.6
1000	119.6	87.0	51.8

The correctness of these thermodynamic values rests entirely upon the correctness of the vibrational assignment used; it is therefore impossible to set an absolute "limit of error." However, unless the vibrational assignment is seriously in error, the principal sources of uncertainty are the three calculated frequencies of the A_2' class. Such errors would be unlikely to change the thermodynamic values by more than 0.5 percent in the most unfavorable case.

Vapor pressure data[1a, 1c] were combined with the thermodynamic values for the gas to give the following data for the liquid: $S^0_{298}(l) = 51.0$, $S^0_{326}(l) = 53.4$ (326°K is the boiling point), $[(F^0-E_0^0)/T]_{298}(l) = -62.5$ cal./mole/degree.

The use of analytical expressions for the thermodynamic properties as functions of the temperature has been discussed by Murphy[15] and by Linnett and Avery.[16] The following expressions are satisfactory over the temperature range of Table VIII:

$$S^0(g) = -19.724 + 32.588 \log T + 0.04164 T$$
$$-[(F^0-E_0^0)/T](g) = -33.877 + 2201.1(1/T)$$
$$+ 32.588 \log T + 0.02082 T$$
$$S^0(l) = -25.062 + 24.582 \log T + 0.05119 T$$
$$-[(F^0-E_0^0)/T](l) = -35.738 + 8869.2(1/T)$$
$$+ 24.582 \log T + 0.02559 T.$$

We wish to express our thanks to Dr. Anton B. Burg for the sample of triborine triamine which made this study possible, and to Professor E. B. Wilson, Jr., who suggested this project and has contributed many helpful suggestions throughout the course of the investigation.

[15] G. M. Murphy, J. Chem. Phys. **5**, 637 (1937).
[16] J. W. Linnett and W. H. Avery, J. Chem. Phys. **6**, 686 (1938).