RECENT CHEMISTRY AND STRUCTURE INVESTIGATION OF NITROGEN TRIIODIDE, TRIBROMIDE, TRICHLORIDE, AND RELATED COMPOUNDS

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I. Introduction

Although new investigations on inorganic nitrogen compounds of chlorine, bromine, and iodine have been reviewed comparatively recently (*28*, *78*), it seems appropriate to discuss the chemistry and structures of nitrogen triiodide, -chloride, and -bromide once more since highly interesting and, in part, surprising results have emerged in the course of the past 2 years.

II. Nitrogen Triiodide

A. POLYMERIC STRUCTURE AND IR SPECTRUM OF NITROGEN TRIIODIDE-1-AMMONIA $(NI_3 \cdot NH_3)_n$

With the elucidation of the structure of nitrogen triiodide-1-ammonia (*58*, *77*), a structural principle, which is widely applicable in both inorganic and organic nitrogen–iodine chemistry, was unexpectedly discovered.

Before this key concept is considered more closely (Sections II, B–F), the structure itself will be described (Fig. 1). It contains a polymeric N—I framework rather than isolated NI_3 units. This is made up of NI_4 tetrahedra joined by common iodine atoms (I1, I1′) into chains of tetrahedra with infinite —N—I—N—I— chains, which are built into sheets of tetrahedra by I—I contacts [I3—I2 neighboring chain (3.36 Å)] between chains lying above one another along the *c*-axis. In many respects the structure of the chain of NI_4 tetrahedra resembles that of SiO_4 tetrahedra in metasilicates. The NI_4 tetrahedra are slightly distorted and have two pairs of equal N—I distances [N1—I1, I1′ (2.30 Å) and N1—I2, I3 (~2.15 Å)]. One iodine atom of each tetrahedron is loosely attached to an ammonia molecule [I2—N2 (2.53 Å)] that projects into the corrugated space between the sheets of tetrahedra (see Fig. 1).

A special characteristic of this structure, in addition to the NI_4 tetrahedra, is the linear or almost linear groups N1—I1′—N1′, N1—I2—N2, and N1—I3—I2 (neighboring chain). This illustrates a

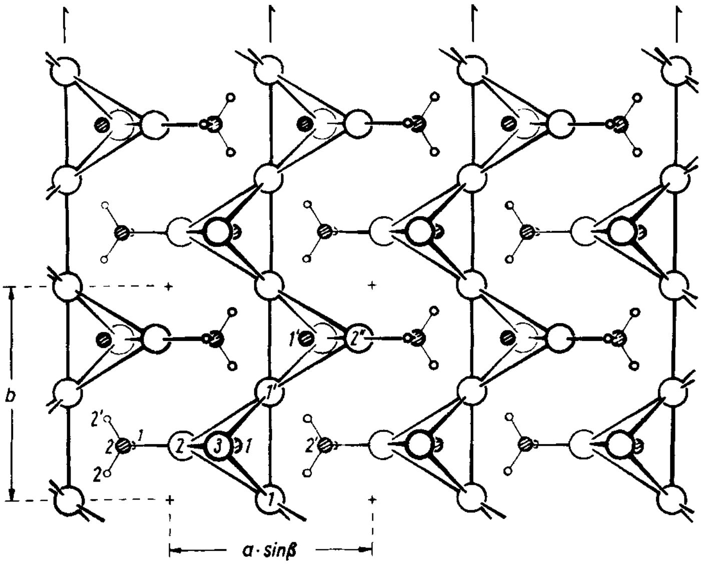


FIG. 1. Projection of the monoclinic crystal structure of nitrogen triiodide-1-ammonia on the (001) plane. Large circles, I atoms; shaded circles, N atoms; small circles, H atoms (*58*).

tendency, which has been observed many times (*100*, *151*, *63*) for covalently bonded iodine atoms, to form a second bond. In fact, it is responsible for the polymeric character of nitrogen triiodide-1-ammonia. The bond in these linear groups of 3 atoms is best described in terms of molecular orbital theory as a 3 center-4 electron bond, using a p orbital of the central iodine and an sp^3 hybrid orbital of each nitrogen, or a p orbital of the second iodine atom (*20*). It is notable that the N1—I1'—N1' group is completely symmetrical, that is, there is no longer a difference between the intramolecular and the intermolecular bond.

Table I shows the IR spectra for the isotopic species $^{14}NI_3 \cdot {}^{14}NH_3$, $^{14}NI_3 \cdot {}^{14}ND_3$, and $^{15}NI_3 \cdot {}^{15}NH_3$. Raman spectra cannot be recorded, even with laser radiation, since the brown–black ammoniate is too rapidly decomposed. Assignment of the bands is difficult because of the polymeric structure of the compound. It was done, after eliminating bands associated with the ammonia in the adduct, by making the simplifying assumption that the polymeric N—I structure is made up of slightly distorted tetrahedra with C_{2v} symmetry, the vibrations of which are not coupled with one another through the relatively heavy

TABLE I

Infrared Spectrum of Nitrogen Triiodide-1-ammonia (*98*)[a]

$NI_3 \cdot NH_3$ (cm^{-1})	$NI_3 \cdot ND_3$ (cm^{-1})	$^{15}NI_3 \cdot {}^{15}NH_3$ (cm^{-1})	Assignment on basis of the tetrahedral model (see text)
3346 w		[b]	ν H—N
3243 w		[b]	ν H—N
1600 w (broad)		[b]	δ H—N—H
1095 m		[b]	δ H—N—H
558 m	556 ss	540 m	ν_{as} N—I2,3
514 m (shoulder)	410 ss	516 m	NH_3 rocking
488 s	491 ss	470 s	ν_s N—I2,3
382 ss	375	371 ss	ν_{as} N—I1
257 ss	237 ss	250 ss	ν $H_3N \cdots I2$
175 w	173 w	174 w	ν_s N—I1
148 s	146 s	148 ss	δ I1—N—I2,3
142 ss	83 ss	148 ?	δ $H_3N \cdots I2$—N
133 ss	131 ss	136 ss	δ I1—N—I1
113 w	113 w	114 w	δ I1—N—I2,3
75–78 ss	68 m	77 ss	δ I2,3—N—I2,3

[a] Intensities: ss, very strong; s, strong; m, medium; w, weak.

[b] The NH bands of $^{15}NI_3 \cdot {}^{15}NH_3$ are the same, to within the accuracy of the measurements, as those of $^{14}NI_3 \cdot {}^{14}NH_3$.

iodine atoms (I1, I1′). Nine normal vibrations would then be expected, eight being IR-active; all these vibrations were found (*98*).

The structural and spectroscopic data make it possible to calculate approximate force constants for the various N—I bonds in nitrogen triiodide-1-ammonia (*98*). In the N1—I1′—N1′ chains, the value for f_{N-I} is 0.81 and that for the N1—I2 or N1—I3 bonds is 1.01 mdyn/Å; for the I2—N2 bond, f_{N-I} is 0.58 mdyn/Å. Table II shows the force constants with the corresponding bond lengths, together with force constants and bond lengths for other nitrogen–iodine compounds. Although force constants were calculated on the basis of different approximations, the expected inverse relationship between the force constant and the bond length is in general fulfilled. This lends support to the values calculated for the force constants. The force constant of the $[I(uro)_2]^+$ cation shows a greater deviation, which may be explained by the fact that the simplifying assumption of a rigid sphere for the ligands on iodine made for the ions $[I(py)_2]^+$, $[I(3\text{-pic})_2]^+$, and $[I(uro)_2]^+$, is no longer correct in the case of urotropin. According to Siebert (*140*), a value of 1.6 mdyn/Å, taking account of the Goubeau

TABLE II

DISTANCES, STRETCHING FORCE CONSTANTS, AND BOND ORDERS OF THE N—I BOND

Compound	r_{N-I} (Å)	f_{N-I} (mdyn/Å)	N_{N-I} (*140*)	References
cis-OSNI	2.03[a]	1.93	1.21	*31*
$NI_3 \cdot NH_3$: N1—I2,3	2.15	1.01	0.63	*58, 98*
$[I(py)_2]^+$	2.16 ± 0.1	1.08	0.68	*64, 56*
$[I(3\text{-pic})_2]^+$	2.24	1.02	0.64	*118, 56*
$(CH_3)_3N \cdot I_2$	2.27	0.87	0.54	*142, 38*
$[I(uro)_2]^+$	2.30	1.13	0.71	*125, 88*
$NI_3 \cdot NH_3$: N1—I1	2.30	0.81	0.51	*58, 98*
$NI_3 \cdot NH_3$: N2—I2	2.53	0.58	0.36	*58, 98*

[a] Sum of covalent radii according to Pauling (*121*).

factor (*51*), is put forward as a theoretical standard for the valence force constant of the N—I bond in nitrogen triiodide (with a free electron pair on nitrogen). From this the bond orders shown in Table II may be calculated (*140*).

In Table III, valence force constants and bond orders for iodides of elements in Group V of the periodic system are compared. Whereas bond orders from phosphorus to bismuth are about unity (monomeric iodides with a predominantly σ-bond character), the values for nitrogen show a significant deviation: Nitrogen triiodide is, indeed, a polymer and has complex bonding relationships (see the foregoing).

The reaction enthalpy for the decomposition reaction of nitrogen triiodide-1-ammonia,

$$2NI_3 \cdot NH_3 \longrightarrow 2NH_3 + N_2 + 3I_2 \qquad (1)$$

TABLE III

STRETCHING FORCE CONSTANTS AND BOND ORDERS OF THE IODIDES OF THE FIFTH MAIN GROUP ELEMENTS

Compound	f_{N-I} (mdyn/Å)	f_1 (mdyn/Å)	N	Ref.
$NI_3 \cdot NH_3$	1.01	1.6	0.63	*98*
	0.81		0.51	
	0.58		0.36	
PI_3	1.21	1.03	1.18	*141*
AsI_3	1.05	0.95	1.11	*141*
SbI_3	0.81	0.75	1.08	*107*
BiI_3	0.65	0.71	0.92	*107*

has been determined with a bomb calorimeter as $\Delta H = -42.1 \pm 2$ kcal/mole (*1*). This value has been used to calculate the N—I bond energy (*1*), although apparently without taking into account the lattice energy and the polymeric character of nitrogen triiodide. (The hypothetical monomeric triiodide has three N—I bonds per unit formula NI_3, whereas the polymer shows four such bonds, of two different lengths, per unit formula.)

B. EXCHANGE STUDIES ON NITROGEN TRIIODIDE-1-AMMONIA WITH ND_3-AMMONIA AND AMMONIA-^{15}N

From the structure of the ammoniate, a relatively easy exchange of the ammonia with other bases (see Section II, E) or isotopically labeled ammonia is to be expected. In experiments involving the condensation of ammonia-^{15}N onto nitrogen triiodide-1-pyridine in order to prepare labeled $NI_3 \cdot {}^{15}NH_3$, the expected product was, surprisingly, not obtained:

$$NI_3 \cdot Py + {}^{15}NH_{3(liq)} \not\rightleftharpoons NI_3 \cdot {}^{15}NH_3 + Py \qquad (2)$$

Instead, ${}^{15}NI_3 \cdot {}^{15}NH_3$ was produced, with exchange also occurring in the NI_4 tetrahedra (N1, Fig. 1). The reverse reaction also fails to give the desired product: Rather, it gives $NI_3 \cdot NH_3$ (*97*):

$$^{15}NI_3 \cdot Py + NH_{3(liq)} \not\rightleftharpoons {}^{15}NI_3 \cdot NH_3 + Py \qquad (3)$$

Since nitrogen triiodide-1-ammonia is only very slightly soluble in liquid ammonia (ca. 1 mg/ml at −75°C) and no dissolution was observed in the experiments, an exchange mechanism other than that involving solution seems likely. To clarify this point exchange experiments between solid nitrogen triiodide-1-ammonia and gaseous ammonia were made and followed by IR spectroscopy (*29*, *30*). They are summarized in Table IV.

The exchange experiments show in the first place that, in absence of a solvent, not only the adduct ammonia (N2, Fig. 1) but also nitrogen in the NI_4 tetrahedra (N1, Fig. 1) can be exchanged. Furthermore, the completeness of the exchange is seen to depend on three factors.

1. The quantity of ammonia available. Experiments 1–3 show that in a static ammonia atmosphere corresponding to a molar ratio of about $NI_3 \cdot NH_{3(solid)} : 2NH_{3(gas)}$, no exchange of the adduct ammonia occurs, whereas, if for the same time a greater excess of ammonia is available in a flow system, exchange of the adduct ammonia is complete. Lack of exchange in a stationary ammonia atmosphere cannot be attributed to too low a diffusion rate of the gaseous ammonia since it has a low molecular weight and a high diffusion coefficient.

TABLE IV

Exchange Experiments between Solid Nitrogen Triiodide-1-ammonia and Gaseous Ammonia at −5°C and Atmospheric Pressure

No.	Starting products[a]		Reaction conditions (hr)	Final product[a]: Nitrogen triiodide-1-ammonia
	Nitrogen triiodide-1-ammonia	Ammonia		
1	$NI_3 \cdot ND_3$, 2	NH_3	Flow, 24	$NI_3 \cdot NH_3$, 4
2	$NI_3 \cdot NH_3$, 2	ND_3	Static, 20	$NI_3 \cdot NH_3$, 4
3	$NI_3 \cdot NH_3$, 2	ND_3	Flow, 24	$NI_3 \cdot NH_3/ND_3$, 4; only a little NH_3
4	$^{15}NI_3 \cdot {}^{15}NH_3$, 2	ND_3	Flow, 5	$^{14/15}NI_3 \cdot {}^{15}NH_3/ND_3$, 4; $^{14}NI_3:{}^{15}NI_3 = 1:2$; $^{15}NH_3:ND_3 = 1:1$
5	$^{15}NI_3 \cdot {}^{15}NH_3$, 2	NH_3	Flow, 0.5	$^{14/15}NI_3 \cdot {}^{14/15}NH_3$; $^{14}NI_3:{}^{15}NI_3 = 1:2$–$3$
6	$^{15}NI_3 \cdot {}^{15}NH_3$, 2	NH_3	Flow, 2	$^{14/15}NI_3 \cdot {}^{14/15}NH_3$; $^{14}NI_3:{}^{15}NI_3 = 1:1$
7	$^{15}NI_3 \cdot {}^{15}NH_3$, 2	NH_3	Flow, 2.25	$^{14/15}NI_3 \cdot {}^{14/15}NH_3$; $^{14}NI_3:{}^{15}NI_3 = 1:1$
8	$^{15}NI_3 \cdot {}^{15}NH_3$, 2	NH_3	Flow, 18	$^{14/15}NI_3 \cdot {}^{14/15}NH_3$; $^{14}NI_3:{}^{15}NI_3 = 1:1$
9	$^{15}NI_3 \cdot {}^{15}NH_3$, 2	NH_3	Flow, 67	$^{14/15}NI_3 \cdot {}^{14/15}NH_3$; $^{14}NI_3:{}^{15}NI_3 = 1:1$; $^{14}NH_3:{}^{15}NH_3$: mainly $^{14}NH_3$
10	$NI_3 \cdot NH_3$, 1	NH_3	Flow, 3.5	$NI_3 \cdot NH_3$, 2
11	$^{15}NI_3 \cdot {}^{15}NH_3$, 1	NH_3	Flow, 2	$^{14/15}NI_3 \cdot {}^{14/15}NH_3$, 2; $^{14}NI_3:{}^{15}NI_3 = 1.5:1$
12	$^{15}NI_3 \cdot {}^{15}NH_3$, 3	NH_3	Flow, 3	$^{15}NI_3 \cdot {}^{14/15}NH_3$; $^{14}NH_3:{}^{15}NH_3 = 1:1$

[a] (1) Poorly crystallized $NI_3 \cdot NH_3$ from dilute solutions of ammonium chloride and iodine chloride by rapid mixing at room temperature; (2) moderately crystallized $NI_3 \cdot NH_3$ from dilute solutions of ammonium chloride and iodine chloride by slow dropwise addition of the latter at 0°C; (3) well-crystallized $NI_3 \cdot NH_3$ from 2 by standing 20 hr in an atmosphere of gaseous ammonia at −5°C; (4) only NH_3/ND_3 exchange detected, no H/D exchange.

2. The duration of the exchange experiment. Experiments 5 and 6 show that nitrogen in the NI_4 tetrahedra is more completely exchanged in an experiment lasting 2 hr than after half an hour. Similarly, exchange of the adduct ammonia has proceeded further after 24 hr than after 5 hr (Experiments 3, 4, and 9).

3. The state of the nitrogen triiodide-1-ammonia crystals. If the experiment is prolonged by several hours, there is no further increase in nitrogen exchange in the NI_4 tetrahedra, whereas exchange of adduct ammonia goes to completion in this time period (Experiments 6–9). Experiment 10 provides the key to this observation, showing that the ammoniate sinters or recrystallizes when exposed to gaseous ammonia: Poorly crystallized material with a high surface area is transformed into material that is visibly more crystalline and of lower surface area. Sintering processes occurring by a gas–solid interaction are already known and have been closely studied for various examples (*67*). Experiments 6, 11, and 12 show that the state of the crystals and their surface area play an important part in the exchange process: Poorly crystalline nitrogen triiodide-1-ammonia of high surface area is able to exchange three-fifths of the compound; moderately crystalline material, a half; and highly crystalline material of low surface area, none of the nitrogen in the NI_4 tetrahedra in comparable times. Exchange of the adduct ammonia, on the other hand, is little influenced by the state of the crystals.

Consequently, we have developed the following picture of the exchange process on a poorly crystalline sample of high surface area.

1. Gaseous ammonia first comes into equilibrium with the surface by an adsorption–desorption process.

2. The adsorbed ammonia (a) by diffusion comes into equilibrium with adduct ammonia between the puckered sheets of the structure and (b) by surface iodine–hydrogen exchange comes into equilibrium with imperfectly formed, energy-rich chains or planes of NI_4 tetrahedra.

3. In parallel with processes 1 and 2, sintering of the ammoniate takes place with a reduction in surface. As a result, process 2b is gradually stopped whereas 2a is at most retarded.

Complete exchange of nitrogen in the NI_4 tetrahedra (N1, Fig. 1) in liquid ammonia (*97*), which has been mentioned previously, can for the time being not be better explained than by postulating a solution mechanism. Complete solution, to be sure, does not seem to be necessary. It is sufficient to assume a superficial solution equilibrium that retards recrystallization and surface area reduction of the nitrogen triiodide-1-ammonia.

C. NITROGEN TRIIODIDE-3-AMMONIA $(NI_3 \cdot 3NH_3)_n$ AND ITS IR SPECTRUM

Nitrogen triiodide-3-ammonia has an IR spectrum at −60°C (*9*) which is very similar to that of the monoammoniate (Table V) (*89*). The similar position of the intense NI skeletal vibrations is especially striking. The spectrum, therefore, leads to the view that NI_4 tetrahedra are again present in this compound and that they resemble those in the monoammoniate in structure and dimensions. In all probability, the NI_3 molecules form infinite chains of linked NI_4 tetrahedra as before. Whether the chains are linked through I—I contacts as for nitrogen triiodide-1-ammonia (see Section II, A) or whether there are isolated chains with the I2 and I3 atoms (Fig. 1) fully coordinated by ammonia cannot be determined from the IR spectrum. The multiple absorptions in the $I—NH_3$ vibrational region (boxed in Table V) leave the possibility open that I—I contacts in the triammoniate are suppressed in favor of $I—NH_3$ contacts. On the other hand, the observation that the crystal form does not change in going from the 3-ammoniate to the 1-ammoniate (*91, 57*) indicates that there is no change in the NI skeleton and that the additional ammonia molecules of the 3-ammoniate are held in lattice cavities, possibly by hydrogen bonds.

D. NITROGEN TRIIODIDE AMMONIATES FORMED BELOW −75°C (MONOIODAMINE-1-AMMONIA AND MONOIODAMINE FORMED BELOW −85°C)

Red–brown (well-crystallized) or black (finely divided) nitrogen triiodide-1-ammonia may be prepared not only directly from aqueous solution (*41*) but also via green iridescent nitrogen triiodide-3-ammonia as an intermediate in, for example, the reaction of iodine with liquid ammonia (*78, 28*). In this case one is restricted by the melting and boiling points of ammonia to the temperature range of −75°C to −35°C. It has been shown earlier by the most diverse experimental methods that only the two nitrogen triiodide ammoniates referred to exist above −75°C (*28, 91*).

The existence of further ammonia adducts stable at lower temperatures was established by the reaction of iodine bromide at −75° to −85°C with a mixed solvent consisting of two parts by volume of chloroform with one of ammonia (*30, 110, 55*). This mixture remains liquid to −95°C. In addition to soluble ammonium bromide, the reaction yields a red precipitate with a nitrogen-to-iodine ratio of 1.5–2.5:1, i.e., a mean of about 2:1. Its low-temperature IR spectrum

TABLE V

Infrared Spectrum of Nitrogen Triiodide-3-ammonia Compared with That of Nitrogen Triiodide-1-ammonia[a]

$NI_3 \cdot NH_3$ (cm^{-1})	$NI_3 \cdot 3NH_3$ at −60°C (cm^{-1})	$NI_3 \cdot 3ND_3$ at −60°C (cm^{-1})	$NI_3 \cdot ND_3$ (cm^{-1})	Assignment on basis of the tetrahedral model
3346 w				ν H—N
3243 w				ν H—N
1600 w (broad)				δ H—N—H
1095 m				δ H—N—H
558 m	579 s	574 ss	556 ss	ν_{as} N—I2,3
514 m (shoulder)	530 ? w	433 ss	410 ss	NH_3 rocking
	512 m (shoulder)			
488 s	506 s	505 s	491 ss	ν_s N—I2,3
382 ss	385 ss	369 w	375	ν_{as} N—I1
257 ss	203–268 ss	200–244 ss	237 ss	ν $H_3N \cdots$ I2
175 w	172 w	164 w	173 w	ν_s N—I1
148 w	141 w	142 w	146 s	δ I1—N—I2,3
142 ss	128 ss	125 m	83 ss	δ $H_3N \cdots$ I2—N
	113 w (shoulder)	110 m		
	101	90 ? m		
		87 ? s		
133 ss	133 m (shoulder)	136 s[b]	131 ss	δ I1—N—I1
		131 s[b]		
113 w	107 m	104 m	113 w	δ I1—N—I2,3
75–78 ss	81–83 ss	77–81 ? ss	68 m	δ I2,3—N—I2,3

[a] Intensities: ss, very strong; s, strong; m, medium; w, weak.

[b] Crystal field splitting ?

TABLE VI

INFRARED SPECTRUM OF NITROGEN TRIIODIDE-CA. 5-AMMONIA AND NITROGEN TRIIODIDE-CA. 2-AMMONIA COMPARED WITH NITROGEN TRIIODIDE-3-AMMONIA AND NITROGEN TRIIODIDE-1-AMMONIA[a]

$NI_3 \cdot NH_3$ (cm^{-1})	$NI_3 \cdot \sim 2NH_3$ ca. -100°C (cm^{-1})	$NI_3 \cdot \sim 5NH_3$ ca. -100°C (cm^{-1})	$NI_3 \cdot 3NH_3$ -60°C (cm^{-1})	Assignment on basis of the tetrahedral model
3346 w				ν H—N
3243 w				ν H—N
1600 w (broad)				δ H—N—H
1095 m				δ H—N—H
558 m	574 m	579 s	579 s	ν_{as} N—I2,3
	543 s			
514 m (shoulder)		515 m (shoulder)	530 ? w	NH_3 rocking
			512 m (shoulder)	
488 s	502 m	506 ss	506 s	ν_s N—I2,3
	483 m			
382 ss	380 ss	385 ss	385 ss	ν_{as} N—I1
257 ss	248 s	200–270 ss	203–268 ss	ν $H_3N \cdots I2$
175 w	174 w	168 w	172 w	ν_s N—I1
148 w	148 w	141 w	141 w	δ I1—N—I2,3
	141 w			
142 ss	124 s	128 s	128 s	δ $H_3N \cdots I2$—N
		113 w	113 w (shoulder)	
		101 w	101 w	
133 ss	132 w	132 m (shoulder)	133 m (shoulder)	δ I1—N—I1
113 w	112 w	107 m	107 m	δ I1—N—I2,3
	105, 103 w			
75–78 ss	89, 81 s	81–83 ss	81–83 ss	δ I2,3—N—I2,3
	79			

[a] Intensities: ss, very strong; s, strong; m, medium; w, weak.

(Table VI) corresponds almost exactly with that of nitrogen triiodide-3-ammonia, the almost identical position of the intense NI skeletal vibration being especially noteworthy. This leads us to suppose that the red compound is a pentammine, $NI_3 \cdot {\sim}5NH_3$ with the same polymeric $(NI_3)_n$ framework.

The relationship between the triammine and the pentammine is also brought out by the observation that the red pentammine is converted into the green triammine above −75°C either in liquid ammonia or in the mixed solvent referred to above. The green compound is also transformed into the red one in the mixed solvent at −75° to −85°C.

Below −85° to −90°C, iodine bromide and the mixed solvent do not give the red pentammine but a second red compound that likewise has a nitrogen-to-iodine ratio of 1.5–2.5:1, although the low-temperature IR spectrum is different. Above −85°C it is transformed into the first red compound, nitrogen triiodide-5-ammonia (*30*, *55*). We believe the second red compound to be monoiodamine-1-ammonia, which is discussed in Section II, L. The existence of two red compounds was not known in earlier publications (*78*, *28*, *91*, *81*, *27*, *79*, *80*), but one can deduce from the temperature during the preparation which compound was obtained.

If a sample of the red pentammine is pumped for several days at −90°C at 10^{-5} Torr or covered with ether and held for 4 hr at −75°C, a black substance is produced with a nitrogen iodine ratio 1.1–1.4:1, that is, approximately 1:1. Its low-temperature IR spectrum (Table VI) shows, in addition to bands of the polymeric 5- or 3-ammoniate, those of the polymeric 1-ammoniate (with some small deviations). We consider the black compound to be a nitrogen triiodide with the mean composition $NI_3 \cdot {\sim}2NH_3$ in which $NI_3 \cdot 3NH_3$ and $NI_3 \cdot NH_3$ structural units are present; the NI_3 skeleton should be polymeric and made up of NI_4 tetrahedra as in the 1-, 3-, and 5-ammoniates (*110*).

Removal of ammonia from the red monoiodamine-1-ammonia in the same way does not result in a black compound with the composition $NI_3 \cdot {\sim}2NH_3$; instead we obtain a second black compound with a reproducible nitrogen-to-iodine ratio of 1:1 and a different low-temperature IR spectrum (*30*). We believe this to be monoiodamine. Authors of earlier publications did not realize that two black compounds existed, and they were, therefore, not differentiated. It is, however, possible to decide which of the two was handled from the temperature during the preparation of the red compound from which ammonia was removed (*78*, *28*, *81*, *27*, *80*).

It is impossible to decide from the IR spectrum how the additional ammonia molecules in the pentammine are bonded to the $(NI_3)_n$ framework (cf. what was said in Section II, C about additional ammonia molecules in the triammine). The ease and speed with which red pentammine is re-formed from the black diammine and ammonia, which is in contrast to the difficult and slow formation of green triammine from the monoammine, leads us to suppose that both of the new polymeric nitrogen triiodide ammines may have a disordered lattice structure with a large surface area and possibly only short $(NI_3)_n$ chains of varying length. The poor reproducibility of the analytical results points to the same conclusions.

E. Adducts of Nitrogen Triiodide with Aprotic N, O, S, and P Bases

As was shown in Section II, B ammonia in nitrogen triiodide-1-ammonia is relatively easily exchanged with isotopically labeled ammonia. A corresponding exchange without change in the polymeric N—I framework is also possible with aprotic N, O, S, and P bases. So far the reaction with tertiary N bases has been most fully investigated.

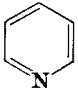
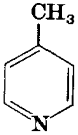
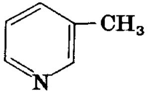
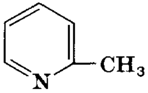
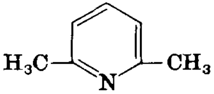
1. *Adducts with Tertiary* N *Bases*

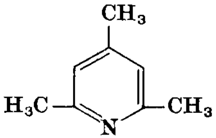
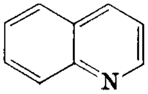
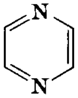
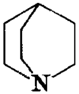
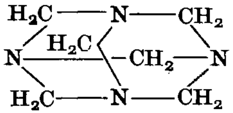
These adducts are usually formed by direct reaction of preformed nitrogen triiodide-1-ammonia with excess of base, with or without additional solvent (usually water), and ammonia is set free. It is almost always possible to work at room temperature or 0°C. It seldom happens that the desired adduct is obtained by adding the base (pyridine, quinuclidine, urotropine) to the reaction mixture in which nitrogen triiodide is being made from ammonia and iodine monochloride or potassium triiodide. The compounds obtained and their properties are shown in Table VII.

The formulas of these adducts are, as a rule, established by the analytically determined ratio of total nitrogen to iodine, which in most cases is 2:3 within experimental error. In the case of nitrogen triiodide-1-pyridine, 1-picoline-4, and 1-quinoline, it is possible to differentiate between inorganic and organic nitrogen: the ratio $N_{inorg}:I:N_{org}$ is 1:3:1, as would be expected (*77*, *147*). In reactions with urotropine and quinuclidine, different ratios were found [urotropine:$N_{inorg}:I:N_{org}$ = 1:5:4 (*82*); total analysis of quinuclidine gives C 13.2, H 2.2, N 3.7, and I 80.2%; $N_{inorg}:I:N_{org}$ = 1:4:1 (*146*, *90*)]. In fact, urotropine forms an adduct with the abnormal composition $NI_3 \cdot I_2 \cdot (CH_2)_6N_4$. Since this is based on a changed polymeric structure, it is discussed

TABLE VII

ADDUCTS OF NITROGEN TRIIODIDE WITH TERTIARY N BASES

Base	Formula	Color	Stability	References
Pyridine 	$NI_3 \cdot C_5H_5N$	Dark brown	25°C decomposition	*77, 62, 147, 7, 61*
	$NI_3 \cdot 3C_5H_5N$?	Green	−30°C decomposition	*77, 7, 146*
Picoline-4 	$NI_3 \cdot CH_3C_5H_4N$		25°C decomposition	*62, 147*
Picoline-3 	$NI_3 \cdot CH_3C_5H_4N$	Brown-black	25°C decomposition	*146, 90*
Picoline-2 	$NI_3 \cdot CH_3C_5H_4N$	Brown-black		*146, 90*
Lutidine 	$NI_3 \cdot (CH_3)_2C_5H_3N$	Brown-black	25°C decomposition	*146, 90*

Collidine 	$NI_3 \cdot (CH_3)_3C_5H_2N$	Brown-black	0°C decomposition	*146, 90*
Quinoline 	$NI_3 \cdot C_9H_7N$ $NI_3 \cdot 3C_9H_7N$?	Green-black	25°C decomposition Light-sensitive 25°C decomposition	*147* *72*
Pyrazine 	$NI_3 \cdot C_4H_4N_2$	Brown-black	25°C decomposition	*145*
Trimethylamine	$NI_3 \cdot (CH_3)_3N$	Black	0°C rapid decomposition	*146, 90*
Triethylamine	$NI_3 \cdot (C_2H_5)_3N$?		0°C inst. decomposition	*146, 90*
Quinuclidine 	$N:I:C_7H_{13}N$ $= 1:4:1$	Black		*146, 90*
Urotropine 	$NI_3 \cdot I_2 \cdot (CH_2)_6N_4$	Red	25°C stable	*82, 124*

later in Section II, I. The nature of the compound formed by quinuclidine has not yet been clarified.

X-Ray powder photographs of nitrogen triiodide-1-pyridine and -1-picoline show both compounds to form monoclinic crystals like those of the 1-ammonia, and to have almost the same angle β as well as b- and c-axes of the unit cells ($\beta = 93°–98°$; $b = 7.5–7.6$, and $c = 6.3–6.4$ Å) (*62*). This indicates that the sheets of NI_4 tetrahedra that extend in the bc plane of the $(NI_3)_n$ framework (cf. Section II, A and Fig. 1) remain practically unchanged in going from the 1-ammoniate to nitrogen triiodide-1-pyridine or 1-picoline-4. On the other hand, the progressive lengthening of the a-axis when ammonia is replaced by pyridine or picoline-4 ($a = 7.1, 10.6, 11.3$ Å) shows the steadily increasing space needed by the base bound to I2 between the puckered sheets of tetrahedra.

Finally, it is shown by a full X-ray structural investigation of the pyridine adduct (Fig. 2) (*61*) that the adducts of nitrogen triiodide with tertiary N bases are structurally very similar to nitrogen triiodide-1-ammonia (Section II, A). Chains of tetrahedra with infinite —N—I—N—I— linkages showing a characteristic translational period of 7.5 Å parallel to the b-axis again occur. The adduct pyridine molecules are bonded through nitrogen (N2) to I2. Table VIII summarizes the corresponding distances and angles. They emphasize the structural

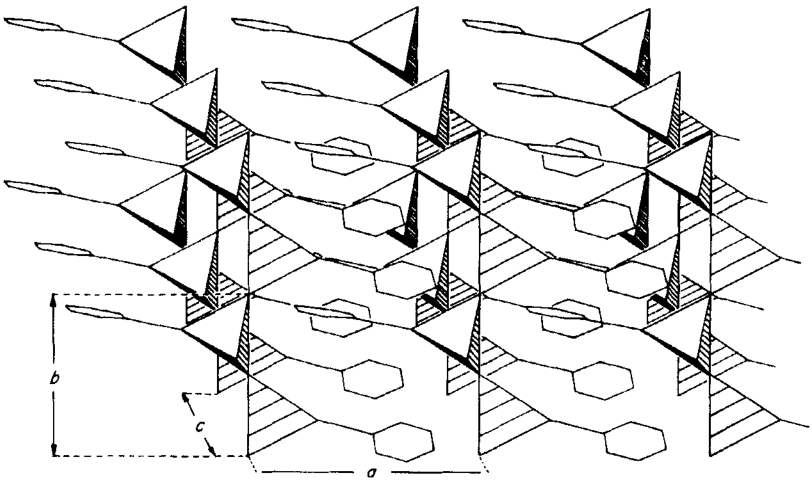


FIG. 2. Spatial representation of the monoclinic structure of nitrogen triiodide-1-pyridine; projection approximately on the (001) plane. In spite of a somewhat different presentation, the analogy of the chain structure of NI_4 tetrahedra with the structure shown in Fig. 1 is apparent. The notation of the N and I atoms of the polymeric N—I framework in Fig. 1 is, therefore, applicable to Fig. 2 (*61*).

TABLE VIII

DISTANCES AND ANGLES IN NITROGEN TRIIODIDE-1-AMMONIA AND -1-PYRIDINE

Distance or angle measured	$NI_3 \cdot C_5H_5N$	$NI_3 \cdot NH_3$
I3—I2 (neighboring chain)	3.93 Å	3.36 Å
N1—I1,I1′	2.36 Å	2.30 Å
N1—I2,I3	~2.10 Å	~2.15 Å
I2—N2	2.59 Å	2.53 Å
N1—I1′—N1′	180°	180°
N1—I2—N2	174°	176°
N1—I3—I2 (neighboring chain)	153°	172°

analogy but also show that in the pyridine adduct the cohesion of the separate chains of tetrahedra to the sheets of tetrahedra in the *bc* plane is not as strong as in the ammonia adduct. The angle N1—I3—I2 (neighboring chain) is distorted to 153° by the bulky pyridine ring and formation of the normally linear 3 center–4 electron bond between the 3 atoms is made more difficult. The iodine–iodine distance (I3—I2, neighboring chain) between the chains of tetrahedra is, as a result, increased from 3.36 to 3.93 Å and can be looked on as only a very weak I—I contact (the sum of the van der Waals radii of 2 iodine atoms is 4.30 Å).

The nitrogen triiodide–tertiary N-base adducts, for which no full X-ray structural analysis is available, may be identified by their IR spectra, besides their dark color, their tendency to explode on shock or friction, and their analyses. The upper part of Table IX shows the spectra of these adducts to exhibit the three strong NI-stretching vibrations at ca. 380, ca. 490, and ca. 560 cm^{-1}, which also occur in the spectrum of nitrogen triiodide-1-ammonia and are characteristic of the NI_4 tetrahedra that make up its polymeric N—I framework. The fourth, less intense, NI-stretching vibration at ca. 170 cm^{-1} and the INI deformation vibrations are, on the other hand, less often firmly assigned, as they partly overlap frequencies of the N base and may also be difficult to observe because of the poor quality of the spectra. Further proof for the formation of a nitrogen triiodide adduct with ammonia replaced by tertiary N base is provided by the absence in the IR spectrum of all the vibrational frequencies of ammonia, especially the very characteristic rocking frequency at 514 cm^{-1}. In their place intense bands associated with the N base occur. These may be displaced, as in their iodine adducts, or may overlap with the bands of the N—I framework.

TABLE IX

INFRARED SPECTRA OF THE N—I FRAMEWORK FOR ADDUCTS OF NITROGEN TRIIODIDE WITH N, O, S, AND P BASES COMPARED WITH NITROGEN TRIIODIDE-1-AMMONIA[a]

Adduct	ν_{as} N—I2,3	ν_s N—I2,3	ν_{as} N—I1	ν_s N—I1	δ I1—N—I2,3	δ I1—N—I1	δ I1—N—I2,3	δ I2,3—N—I2,3	Refs.
$NI_3 \cdot NH_3$	558	488	382	175	148	133	113	75–78	*98*
NI_3·pyridine	567	486	372	164	(135)	127	82	70 sh	*98*
NI_3·3pyridine?	575	500	384	ca. 175		127	72 sh	70	*7, 77*
NI_3·picoline-3	560	504	374						*146*
NI_3·picoline-2	556	495	369						*146*
NI_3·lutidine	562	(481)	388						*146*
NI_3·collidine, −40°C	564	500	394						*146*
NI_3·3quinoline?	566	510	380			137			*77, 72*
NI_3·pyrazine	564	503	384						*145*
NI_3·trimethylamine	(562)	(486)	(386)						*146*
x-$NI_3 \cdot y$-dinitrophenolate?	553	482	375						*53*
NI_3·5.5pyridine-*N*-oxide, −40°C	(551)	489	368						*53*
NI_3·2.5tetrahydrofuran, −40°C	563	~500	388	162	142				*53*
NI_3·2.5dioxane-1.4	573	509	377	(163)	145	130 134	103	82	*53*
NI_3·2.5thiophane, −40°C	563	506	375						*53*
NI_3·0.5dithiane, −40°C	558	480	369	169 sh					*53*

[a] Values expressed per [cm^{-1}].

The IR spectrum of the compound with quinuclidine (see above and Table VII) differs considerably from the spectra shown in Table IX; consequently, the structure of this compound cannot yet be predicted.

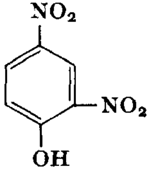
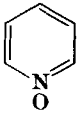
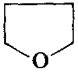
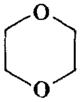
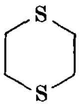
Decomposition of the nitrogen triiodide–tertiary N-base adducts generally leads to the more stable adducts of iodine itself with the tertiary base. Thus, nitrogen triiodide-1-picoline-3 or 1-trimethylamine in aqueous suspension at 0°C is transformed after a time into red-brown diiodine-1-picoline-3, $I_2 \cdot$pic-3, or yellow diiodine-1-trimethylamine, $I_2 \cdot N(CH_3)_3$. The color and IR spectrum of the former lead us to suppose that it is bispicoline-3-iodonium triiodide, $[I(\text{pic-3})_2]^+I_3^-$. Attempts to obtain crystals of the compound with quinuclidine, the nature of which has not been elucidated (see above and Table VII) resulted, apparently because of the duration of the experiments, in yellow diiodine-1-quinuclidine, $I_2 \cdot$quin, or blue-black needle-shaped crystals of quinuclidinium pentaiodide, $[\text{quin} \cdot H]^+I_5^-$. The latter has an interesting structure with infinite iodine chains made up of I_3^- ions and I_2 molecules (*90*) and is transformed at 25°C within weeks into a red-brown substance, presumably quinuclidinium triiodide, $(\text{quin} \cdot H)^+I_3^-$. Clearly, formation of the I_2–base adduct from the NI_3–base adduct is more favored as the base becomes stronger. In the case of adduct $NI_3 \cdot N(C_2H_5)_3$, decomposition in aqueous suspension at 0°C yields iodoform in a few minutes—possibly via adduct $I_2 \cdot N(C_2H_5)_3$.

2. *Adducts with Aprotic* O, S, *and* P *Bases*

A dinitrophenol or dioxane adduct may be obtained from aqueous solution by the general synthetic methods given in Section II, E, 1. For the latter, it is necessary to add hydrochloric acid in order to bring about replacement of the strongly basic ammonia by weakly basic dioxane. Experiments designed to replace ammonia in nitrogen triiodide-1-ammonia by excess of the basic oxalate or acetate anion were unsuccessful. The other adducts shown in Table X are either markedly more temperature-sensitive or are derived from bases that are insoluble in water, so that their synthesis from aqueous solution at $\geqslant 0$°C is impossible. In these cases they are obtained by addition of the base during the synthesis of nitrogen triiodide in methylene chloride at −40°C. It is necessary to make sure that there is always a deficiency of ammonia, so that it does not compete as an adduct molecule with the more weakly basic O, S, or P base. Even under these favorable conditions, however, thiophene is not incorporated into the nitrogen triiodide framework.

TABLE X

ADDUCTS OF NITROGEN TRIIODIDE WITH APROTIC O, S, AND P BASES

Base	Formula	Color	Stability	References
2,4-Dinitrophenol 	$x\text{-}NI_3 \cdot y\text{-}(O_2N)_2C_6H_3ONH_4$?	Black	25°C decomposes	*53*
Pyridine-*N*-oxide 	$NI_3 \cdot {\sim}5.5C_5H_5NO$	Black	> −40°C decomposes	*53*
Tetrahydrofuran 	$NI_3 \cdot {\sim}2.5C_4H_8O$	Black	> −40°C decomposes	*53*
1,4-Dioxane 	$NI_3 \cdot {\sim}2.5C_4H_8O_2$		25°C decomposes	*53*
Thiophane 	$NI_3 \cdot {\sim}2.5C_4H_8S$	Black	> −40°C decomposes rapidly	*53*
1,4-Dithiane 	$NI_3 \cdot {\sim}0.5C_4H_8S_2$	Black	> −40°C decomposes	*53*
Triphenylphosphine	$NI_3 \cdot {\sim}0.5(C_6H_5)_3P$	Black	> −40°C very unstable	*53*

In almost all instances it may be shown by an analytical determination of the N:I ratio that true nitrogen triiodide adducts are formed; a ratio of 1N:3I is found, as expected, although products obtained from methylene chloride are, from the synthesis, still contaminated with ammonium chloride. The proportion of O, S, or P base found by analysis (relative to iodine) or by gas chromatography has so far been determined for only one sample and is, therefore, not certain; variations in the value obtained from base to base could be an indication of the large surface area and the much distorted lattice structure of the nitrogen triiodide sample (cf. Section II, D).

Infrared spectra in the lower part of Table IX are also indicative of the formation of adducts with O, S, and P bases, as are analytical data, black color and shock or friction sensitivity of the compounds. Three strong N—I stretching vibrations at ca. 380, ca. 490, and ca. 560 cm^{-1} again occur for these compounds, although vibrations associated with ammonia are missing and in their place we found vibrations associated with the adduct base, which are in part displaced.

The compounds studied decompose much more readily to iodine or iodinated compounds than the adducts with tertiary N bases described above. Thus, there is an accelerated decomposition of an aqueous suspension of nitrogen triiodide-1-ammonia at room temperature in presence of tetrahydrofuran, thiophane, or triphenylphosphine. The reaction product from the last of these is triphenylphosphine diiodide, Ph_3PI_2; it is not possible first to detect or isolate nitrogen triiodide adducts with the three bases. Only by lowering the temperature to $-40°C$ can one isolate the corresponding adducts by adding the corresponding base to the reaction mixture for the synthesis of nitrogen triiodide in nonaqueous solution. On warming, there is gas evolution from the tetrahydrofuran adduct, and iodine separates, whereas, on warming the solution used for synthesizing the thiophane adduct, a red-violet crystalline substance is obtained (C 16.9, H 2.9, S 11.1, I 67.7, and N 2.2%). Its structure is not known at present. Under the most favorable conditions at low temperature, triphenylphosphine gives a very unstable adduct in low yield, the greater part of the triphenylphosphine being converted to Ph_3PICl.

It cannot be excluded from these observations that the rapid decomposition with nitrogen evolution of an aqueous suspension of nitrogen triiodide-1-ammonia at room temperature in the presence of *p*-nitrophenol (producing yellow 2,6-diiodo-4-nitro- phenol), cyanide, or thiocyanate (producing iodine with iodine cyanide or thiocyanate as intermediates) stems from the formation of very unstable adducts of these bases with nitrogen triiodide, which cannot be isolated. In the case of *p*-nitrophenol, this assumption is supported by the isolation of an adduct with the weaker "base" 2,4-dinitrophenol under the same conditions (see above and Table X).

F. Polymeric Nitrogen Triiodide Structural Analogs from Diiodomethylamine, CH_3NI_2, and *N*,*N*′-Tetraiodoethylenediamine, $I_2NCH_2CH_2NI_2$

These compounds show the same structural analogy to nitrogen triiodide as all of the compounds so far described, although at first sight this would not be expected from their formulas (*81*, *84*, *148*, *85*). Red-brown microcrystalline diiodomethylamine may be obtained from methylamine and iodine or iodine chloride in aqueous solution at 0°C or from the anhydrous amine and iodine or *N*-iodosuccinimide at lower temperatures. Its adducts with pyridine (brick red), trimethylamine (reddish yellow), and methylamine [reddish yellow; this is not CH_3NHI, as was previously supposed (*78*, *133*) but $CH_3NI_2 \cdot CH_3NH_2$ (*28*, *81*)] are prepared by pouring or condensing the base onto diiodomethylamine or nitrogen triiodide-1-ammonia at −15° to −75°C. The red-violet *N*,*N*′-tetraiodoethylenediamine is made by iodination of the diamine with nitrogen triiodide-1-ammonia or iodine chloride at 0°C (cf. Section II, L, 2). The formulas are established by N:I ratio analysis.

The most probable structure for monomeric diiodomethylamine (without adduct molecules) would have a trigonal pyramid with C_s symmetry for the C—N—I framework; six infrared active normal vibrations would then be expected. In a polymeric structure it is likely that the C—N—I framework would, like that of nitrogen triiodide-1-ammonia, be made up of I2CNI1I1′ tetrahedra with C_s symmetry. These would be lined up through common I1,I1′ atoms into infinite chains (Fig. 3). In this case, nine infrared active normal vibrations would

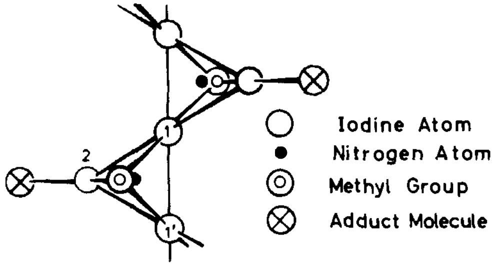


Fig. 3. Section of the chain of tetrahedra for the polymeric diiodomethylamine adduct (*84*).

be expected if we neglect vibrational coupling between the separate tetrahedra through the relatively heavy iodine atoms (I1,I1′) as we did for nitrogen triiodide-1-ammonia.

The compounds and the IR spectra associated with their C—N—I frameworks are shown in Table XI. In so far as they have been measured, nine absorptions are found for the diiodomethylamines, with little difference between the parent compound and its adducts. We must, therefore, conclude that (a) the diiodomethylamines have a polymeric structure and (b), as for nitrogen triiodide, there is no essential structural difference between the amine and its adducts.

Table XI also shows clearly the close relationship between the spectra of the diiodomethylamines and nitrogen triiodide-1-ammonia. Replacement of a heavy iodine atom by a light methyl group results in a frequency increase for the four stretching vibrations. For the bending vibrations, an increase occurs only where I—N—C angles are involved (instead of I—N—I). In addition, the diiodomethylamines exhibit an infrared-active torsional vibration that is missing for nitrogen triiodide-1-ammonia. The relationship between the spectra shows the principle underlying the polymeric structure to be the same in both substances.

X-Ray structural analysis of diiodomethylamine-0.5-pyridine, which is still incomplete, shows there to be a monoclinic unit cell with a translational period of 7.50 Å parallel to the *b*-axis characteristic of the infinite —N—I—N—I—N— chains. It establishes the identity of the polymer structural type in this compound and nitrogen triiodide-1-ammonia. Figure 4 shows a view of the structure in the direction of these infinite —N—I—N—I—N— chains. One can recognize two tetrahedra of an infinite chain of tetrahedra; in fact, they lie obliquely under one another.

It is evident from Table XI that, for the C—N—I framework of *N*,*N*′-tetraiodoethylenediamine, there are nine absorptions if C—C vibrations are omitted and the CN-stretching vibration, which appears as a doublet, is counted as one. Only unimportant displacements in relation to diiodomethylamine and its adducts with N bases are observed. As for them, the infrared spectrum may be explained in terms of I2CNI1I1 tetrahedra with C_s symmetry that are arranged in one direction in infinite chains with common I1 atoms and are bound together in the other direction through methylene groups (Fig. 5). Vibrational coupling between separate tetrahedra through the relatively heavy iodine atoms I1 may again be neglected. Thus for *N*,*N*′-tetraiodoethylenediamine the same polymer structural principle prevails as in nitrogen triiodide-1-ammonia and in the other compounds that have been discussed.

TABLE XI

INFRARED SPECTRUM OF THE C—N—I (OR N—I) FRAMEWORK OF DIIODOMETHYLAMINE, ITS ADDUCTS WITH N BASES, AND OF *N,N'*-TETRAIODOETHYLENEDIAMINE COMPARED WITH NITROGEN TRIIODIDE-1-AMMONIA

CH_3NI_2 (cm^{-1})	$CH_3NI_2 \cdot Py$ (cm^{-1})	$CH_3NI_2 \cdot \frac{1}{2}Py$ (cm^{-1})	$CH_3NI_2 \cdot (CH_3)_3N$ (cm^{-1})	$CH_3NI_2 \cdot CH_3NH_2$ (cm^{-1})	$I_2NCH_2—CH_2NI_2$ (cm^{-1})	Proposed assignment	$NI_3 \cdot NH_3$ (cm^{-1})	Assignment on basis of the tetrahedral model
970	980	(960)	975	990	1045 990	ν N—C	558	ν_{as} N—I2,3
545	544	540[a] 525[a]	518	535	520	ν N—I2	488	ν_s N—I2,3
415	404	385[b]	382	414	405	ν_{as} N—I1	382	ν_{as} N—I1
346	(349)	(350)	320	345	303[c]	ν_s N—I1	175	ν_s N—I1
193[d]	[e]	[e]	[e]	194[d]	187	δ I1—N—C	148	δ I1—N—I2,3
162[d]	[e]	[e]	[e]	169[d]	173	τ Torsion		
133[d]	[e]	[e]	[e]	135[a,d] 131[a,d]	141	δ I1—N—I1	133	δ I1—N—I1
113[d]	[e]	[e]	[e]	125[d]	131	δ I1—N—I2	113	δ I1—N—I2,3
234	230	231	225	226	232	δ I2—N—C	75	δ I2,3—N—I2,3

[a] Crystal field splitting possible.

[b] A further weak band occurs at 470 cm^{-1}.

[c] H_2O band?

[d] Measured at −60°C.

[e] Not measured.

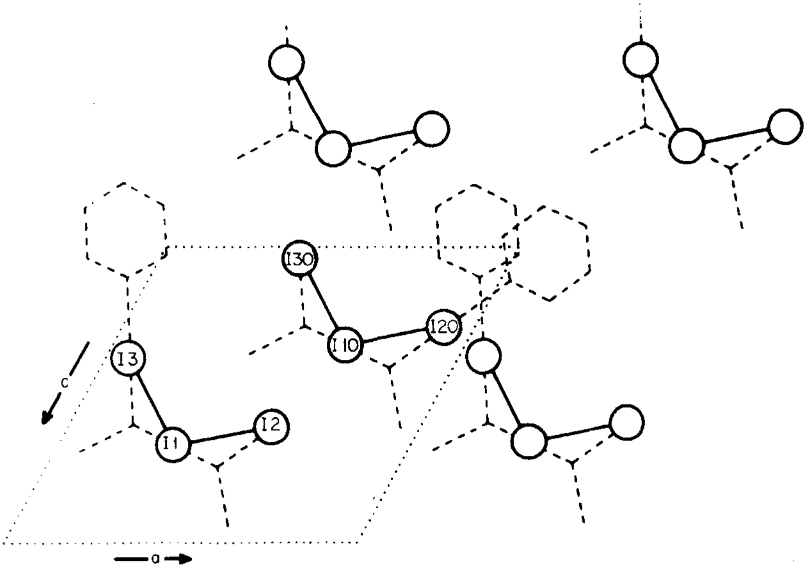


FIG. 4. Projection of the proposed structure for monoclinic diiodomethylamine-0.5-pyridine on the (010) plane. The iodine positions, shown by full lines, are definite; final predictions for the nitrogen and carbon positions cannot yet be made (dashed lines) (*148*).

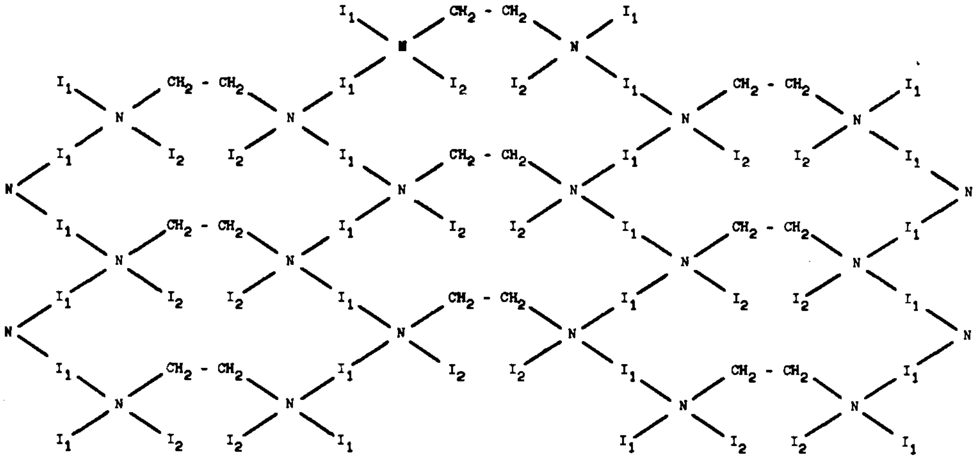


FIG. 5. Proposed structure for *N,N'*-tetraiodoethylenediamine (*85*).

The properties of diiodomethylamine and of *N*,*N'*-tetraiodoethylenediamine so far known are in accord with the polymeric structure. Both are difficultly soluble in all available solvents or dissolve with decomposition. The deep color of these compounds is indicative of iodine–iodine contacts between the chains of tetrahedra as proved for nitrogen triiodide-1-ammonia (see Section II, A). If these contacts are disturbed by adduct formation with N bases, as in nitrogen triiodide-3-ammonia (Section II, C) or in the adducts of diiodomethylamine with pyridine, trimethylamine, or methylamine (see above), the color becomes lighter.

G. MODIFICATION OF THE POLYMERIC STRUCTURAL PRINCIPLE OF NITROGEN TRIIODIDE BY PARTIAL REPLACEMENT OF IODINE: IODODIMETHYLAMINE, $(CH_3)_2NI$

When three iodine atoms are bonded to nitrogen, as in the hypothetical monomer of nitrogen triiodide, the compound stabilizes itself by polymerization as we have seen in Section II, A: The N atom in the monomer with its free pair of electrons acts as an electron donor, with one of the iodine atoms as acceptor, in an acid–base reaction. The same tendency to stabilize by polymerization also arises if only 2 iodine atoms are bonded to nitrogen, the third being replaced by a methyl group (Section II, F illustrates this with the example of diiodomethylamine, its N-base adducts, and *N*,*N'*-tetraiodoethylenediamine). When 1 atom of iodine and two methyl groups are bonded to a nitrogen atom, polymerization according to the same principle is still conceivable, but obviously does not take place (*84*, *146*, *81*).

Yellow microcrystalline iodomethylamine is prepared from the amine and iodine or iodine chloride in aqueous solution at 0°C or, better, because of the temperature sensitivity, in aqueous methanol at −35°C. In a very elegant preparative method the anhydrous amine is iodinated with nitrogen triiodide-1-ammonia, which may be replaced by *N*-iodosuccinimide or iodine, at −55° to −75°C (cf. Section II, L, 2). Crystalline iododimethylamine may also be made in chloroform at −60°C by the following reaction:

$$(CH_3)_3SiN(CH_3)_2 + ICl \longrightarrow (CH_3)_2NI + (CH_3)_3SiCl \qquad (4)$$

Its formula may be established by N:I ratio analysis. It is soluble in dimethylamine, methylene chloride, and chloroform and does not exist in a brown form (*59*) as was previously assumed (*120*).

The solubility and light color show that stable polymerization and iodine–iodine contacts are unlikely, and the IR spectrum confirms this fact. One would expect six, infrared, active normal vibrations for the monomer (trigonal pyramid with C_s symmetry), whereas for the polymer there would be eight associated with the C—N—I framework, neglecting vibrational coupling between the separate tetrahedra (CCNII tetrahedra with C_{2v} symmetry). The spectrum (Table XII) does in fact show eight bands, but only one N—I stretching vibration at 467 cm^{-1}. In addition, in view of the replacement of 2 iodine atoms of the NI_4 tetrahedral unit by lighter methyl groups, the two bands below 100 cm^{-1} are at too low values to be deformation frequencies and must be attributed to lattice vibrations or, at the most, very weak intermolecular N···I contacts. Thus the IR spectrum is more in keeping with a monomolecular structure. Proposed assignments for the remaining six bands correspond with this model. A structure is suggested in Fig. 6. Only by X-ray studies will it be possible to settle finally whether or not there are weak intermolecular N···I contacts.

TABLE XII

INFRARED SPECTRUM OF THE C—N—I FRAMEWORK OF IODODIMETHYLAMINE (SOLID)

Band position (cm^{-1})	Proposed assignment
1030	ν N—C
884	ν N—C
467	ν N—I
266	δ C—N—C
166	δ I—N—C
149	δ I—N—C
92 67	Lattice vibrations ? ν N···I— ?

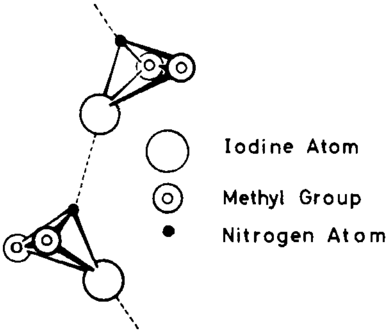


FIG. 6. Proposed structure for iododimethylamine (*84*).

H. IODINE ADDUCTS OF DIIODOMETHYLAMINE AND IODODIMETHYLAMINE

Stabilization of nitrogen triiodide and diiodomethylamine by polymerization to —N—I—N—I—N— chains raises the question of whether the electron-donor nitrogen atom in the iodamines is also able to add on molecular iodine as an electron acceptor and thus to stabilize the iodamines. Are there compounds such as $I_3N—I_2—NI_3$, $I_3N—I_2$, $CH_3I_2N—I_2—NI_2CH_3$, $CH_3I_2N—I_2$, $(CH_3)_2IN—I_2—NI(CH_3)_2$, or $(CH_3)_2IN—I_2$?

A urotropine-stabilized compound of formula $I_3N—I_2$ is reported in Section II, I. It may be mentioned at this point that it is possible to prepare iodine complexes of diiodomethylamine and iododimethylamine (*99*). Bright red 2-diiodomethylamine-1-diiodine, $(CH_3NI_2)_2 \cdot I_2$, and ochre-colored 2-iododimethylamine-1-diiodine, $[(CH_3)_2NI]_2 \cdot I_2$, are obtained from the free amine and excess iodine in aqueous solution at 0°C. Bright red-brown iododimethylamine-1-diiodine, $(CH_3)_2NI \cdot I_2$, may be prepared from iododimethylamine and an excess of ethereal iodine solution at −25°C, although it is not possible to obtain diiodomethylamine-1-diiodine, $CH_3NI_2 \cdot I_2$, in this way.

Analysis of these three compounds gives N:I values of 1:3 (2-diiodomethylamine-1-diiodine), 1:2 (2-iododimethylamine-1-diiodine), and 1:3 (iododimethylamine-1-diiodine). Both of the first two complexes are appreciably more stable thermally than the corresponding simple nitrogen–iodine compounds and may be stored for weeks at −30°C without decomposition.

According to detailed investigations that have already been mentioned (*63*), complexes of this type always have a linear structure, which is in full accord with results referred to above. Either a 2:1 complex, corresponding with $D \cdots X—X \cdots D$, or a 1:1 complex corresponding with $D \cdots X—X$ is formed (D = donor atom; X—X = elemental halogen). Which complex is formed depends on the donor or acceptor strength of the two partners forming the complex. For stronger donor–acceptor interaction, the 1:1 type appears to be preferred, whereas weaker interaction leads to the 2:1 type. A closely similar relationship is found for the complexes considered here: The strong donor trimethylamine forms only the 1:1 complex, whereas for diiodomethylamine, which is a weaker donor, only the 2:1 complex results. With iododimethylamine, which is of intermediate strength, both the 1:1 and the (less stable) 2:1 complexes are able to form. Figure 7 shows the structures proposed for the three iodo complexes (according to Ref. *63* and the results referred to above).

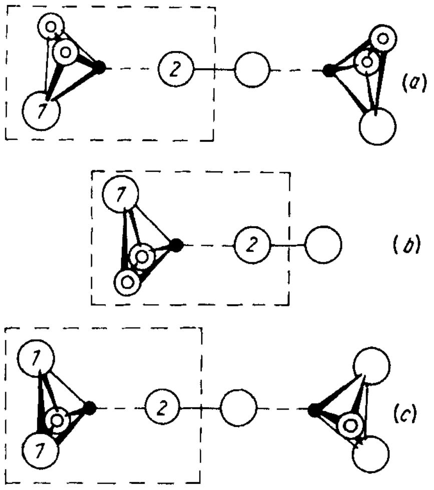


FIG. 7. Proposed structures for 2-iododimethylamine-1-diiodine (a), iododimethylamine-1-diiodine (b), and 2-diiodomethylamine-1-diiodine (c) (*99*).

Infrared spectra may be discussed on the basis of the structures proposed in Fig. 7, assuming CCNI1I2 or I1I1NCI2 tetrahedra with C_s symmetry and neglecting vibrational coupling through the heavy iodine atoms (*99*). This leads to assignments for the vibrational frequencies of 2-diiodomethylamine-1-diiodine with greater ease than in the case of the two iodine adducts of iododimethylamine. Final verification of these proposed structures will depend on X-ray structural analysis.

I. Modification of the Polymeric Structural Principle of Nitrogen Triiodide by Bulky Adduct Bases: Nitrogen Triiodide-1-diiodine-1-urotropine, $NI_3 \cdot I_2 \cdot C_6H_{12}N_4$

It is impossible to insert urotropine into the puckered cavities of polymeric nitrogen triiodide, using the methods mentioned in Section II, E, because the molecule is too bulky for this to occur. An adduct compound, which analysis shows to be $NI_3 \cdot I_2 \cdot$ urotropine is first formed in addition to diiodine urotropine, $I_2 \cdot$urotropine, when part of the nitrogen triiodide-1-ammonia has decomposed, setting free iodine. The principle underlying its structure is, however, different from that in the nitrogen triiodide adducts discussed so far (*82*, *124*).

Brick red nitrogen triiodide-1-diiodine-1-urotropine is the most stable nitrogen triiodide adduct so far described; it explodes only on

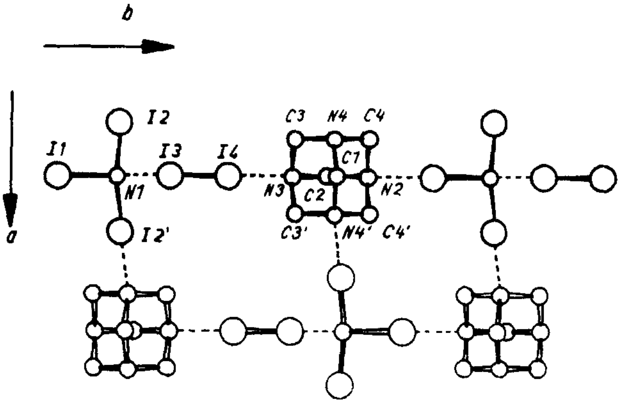


FIG. 8. Projection of the rhombic structure of nitrogen triiodide-1-diiodine-1-urotropine on the (001) plane. Intermolecular bonds are shown by dashed lines (*124*).

impact, under pressure, or when heated. It is also insoluble in all the usual solvents, and, on treatment with an alkaline aqueous ammonia-(pyridine) solution, nitrogen triiodide-1-ammonia (-1-pyridine) is formed instantly.

The crystal structure (Fig. 8) shows the nitrogen triiodide and urotropine molecules to be approximately tetrahedrally surrounded by 4 molecules of another sort. Iodine molecules make up one of the four links between nitrogen triiodide and urotropine. The geometrical arrangement and distances (Table XIII) indicate that there is marked intermolecular bonding between the iodine atoms of nitrogen triiodide and nitrogen atoms in urotropine (I1—N2, I2—N4′, I2′—N4). In

TABLE XIII

DISTANCES AND BOND ANGLES IN NITROGEN TRIIODIDE-1-DIIODINE-1-UROTROPINE

N1—I1	2.14 Å	N1—I3	2.47 Å
N1—I2	2.14 Å	N3—I4	3.23 Å
		N2—I1	2.58 Å
I3—I4	2.81 Å	N4′—I2	2.57 Å
Sum of the covalent radii according to Pauling (*121*)		N + I	2.03 Å
		I + I	2.66 Å
Sum of the van der Waals radii according to Pauling (*121*)		N + I	3.65 Å
		I + I	4.30 Å
N1—I1—N2	175°	N1—I3—I4	175°
N1—I2—N4′	179°	I3—I4—N3	178°

addition, the nitrogen atom of the triiodide shows intermolecular bonding to the iodine molecule (N1—I3), which, in turn, is similarly bonded to the urotropine molecule (I4—N3). The resemblance to the structure of iodoform-1-urotropine is apparent (*21*).

The intermolecular contacts shown result in tetrahedral coordination of 4 iodine atoms (sp^3 hybridization) round the nitrogen of the triiodide (N1). Although the principle underlying the structure of the new compound differs from that of the compounds discussed in Sections II, A–F and H, the tetrahedral structural element [NI_4, $NI_3(CH_3)$, $NI_2(CH_3)_2$] occurs once more. There are, of course, two pairs of almost equal N—I distances in the NI_4 tetrahedra of nitrogen triiodide-1-ammonia and -1-pyridine, whereas NI_4 tetrahedra in nitrogen triiodide-1-diiodine-1-urotropine have three such distances that are almost equal and one that is longer.

In spite of the changed principle underlying the structure, twofold coordination of the iodine atom is maintained as a structural element: All four iodine atoms I1, I2, I3, and I4 have twofold coordination and their bond angles are approximately 180° (3 center–4 electron bond; cf. Section II, K).

J. MODIFICATION OF THE POLYMERIC STRUCTURAL PRINCIPLE OF NITROGEN TRIIODIDE BY CHANGE IN THE sp^3 HYBRIDIZATION AT NITROGEN: *N*-DIIODOFORMAMIDE, $HCONI_2$

In diiodoformamide, a red, needle-shaped crystalline substance slowly decomposing at room temperature (*49*), there are two fundamental changes in comparison with the compounds discussed so far: Nitrogen shows sp^2 instead of sp^3 hybridization and oxygen is an additional donor. It is thus no longer possible to have tetrahedral coordination round nitrogen, and the acceptor, iodine, can attain its coordination number of 2 only through donation from oxygen.

The crystal structure (*123*) (Fig. 9) shows in fact that, of the structural elements so far encountered, only the almost linear twofold coordination of iodine is operative. Each diiodoformamide molecule contains two acceptor (the iodine atoms) and two donor functions (both free electron pairs on oxygen), which is not unlike the situation in formamide itself (*103*). The molecules combine to form staggered chains along the *a*-axis through I2 and O, the N—I2—O group being almost linear (Table XIV). In addition, each molecule possesses a free donor and acceptor site, which lie on different sides of the chain and through which the chains are joined up into sheets lying at right angles to the *b*-axis. Complete linearity of the N—I1—O group is, however,

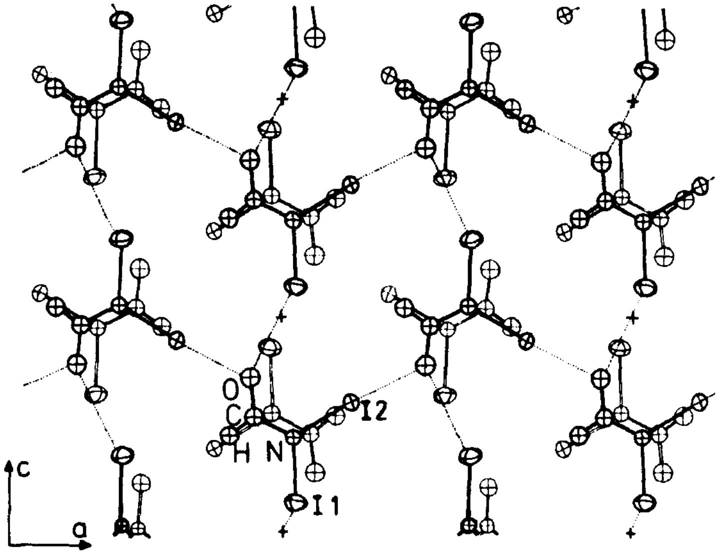


FIG. 9. Projection of the rhombic structure of *N*-diiodoformamide on the (010) plane. Atoms shown in heavy print lie at $y = 0.25$; the other atoms shown are at $y = -0.25$. Intermolecular bonds for $y = 0.25$ are shown by dotted lines (*123*).

impossible on geometrical grounds. The structure observed represents the best possible arrangement of all O—I1 bonds between neighboring chains. The unfavorable form of the grouping results in a weakening of the intermolecular O—I1 bond compared with the O—I2 bond (Table XIV). Distances between atoms of different layers are almost always greater than the sum of the van der Waals radii. The position of the layers in relation to one another is determined by optimum packing of the large iodine atoms.

TABLE XIV

DISTANCES AND BOND ANGLES IN *N*-DIIODOFORMAMIDE

N—I1	2.04 Å	I1—N—I2	119°
N—I2	2.10 Å	N—I2—O	171°
O—I2	2.57 Å	N—I1—O	151°
O—I1	3.13 Å		
I1—I2	3.56 Å		
Sum of the covalent radii according to Pauling (*121*)		O + I	1.99 Å
Sum of the van der Waals radii according to Pauling (*121*)		O + I	3.55 Å

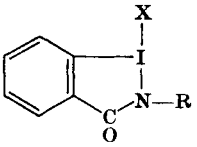
K. Linear Twofold Coordination of Iodine as an Essential Structural Element in Solid Nitrogen–Iodine Compounds

That linear twofold coordination of iodine is the essential structural feature for stabilizing nitrogen–iodine compounds is again illustrated in Table XV (*124*). It occurs in all structures that have been investigated so far. Distances *d*1 and *d*2 never exceed the sum of the van der Waals radii, and the bond angle at the central iodine atom always lies in the region of 180°.

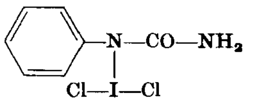
Bond lengths *d*1 and *d*2, which change inversely with bond strength, depend on the donor strengths of X1 and X2 and on the geometry of the group X1—I—X2. For example, the stronger and shorter *d*1 becomes because of the high donor strength of X1 and a favorable geometry, the weaker and longer *d*2 will be. It is, however, not possible at present to make a quantitative comparison of *d*1 with *d*2 because of the paucity of structural data and the variable nature of both the donor X[N, O, I] and the geometry. In the case of interhalogen compounds and adducts of iodine halides, an attempt has been made to introduce reduced radii *R*1 and *R*2 for the iodine atom in the two bonds of the X1—I—X2 group and then to establish experimentally a relationship between the two radii (*65*). Only some of the nitrogen–iodine compounds satisfy this relationship, however, and, because of the paucity of data, it is not possible to determine what is responsible for the deviations.

In describing the bond, a simplified MO model is used, namely, the 3 center–4 electron bond, which has led to good results for the interhalogen compounds. Qualitative predictions based on this model are as well fulfilled for nitrogen–iodine compounds as for iodine adducts.

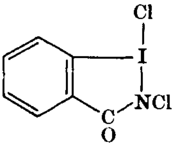
A bond angle of ~180° at iodine is also encountered together with angles of ~90° in structural studies of polyvalent organic iodine compounds such as phenyl iodine dichloride, $C_6H_5ICl_2$, and diphenyliodonium chloride, $(C_6H_5)_2ICl$ (*4*). These angles suggest that 3 center–4 electron bonds are again involved, with the participation of only *p* orbitals of the iodine atom. It may, therefore, be expected that in recently discovered polyvalent iodine–nitrogen compounds, such as the benziodazoles (I) (*153*, *5*) and the iododichloridamines (II) (*23*), there



(I)



(II)



(III)

TABLE XV

TWOFOLD COORDINATION OF IODINE IN THE CRYSTAL STRUCTURE OF NITROGEN–IODINE COMPOUNDS STUDIED[a]

Compound	Grouping $X1\overset{d1}{\text{—}}I\overset{d2}{\text{—}}X2$	$d1$ (Å)	$d2$ (Å)	Angle (°)	Section	Figure
$(NI_3\cdot py)_n$	N1—I1′—N1′	2.36	2.36	180	II, E	2
	N1—I2—N2	~2.10	2.59	174		
	N1—I3—I2 (neighboring chain)	~2.10	3.93	153		
$(NI_3\cdot NH_3)_n$	N1—I1′—N1′	2.30	2.30	180	II, A	1
	N1—I2—N2	~2.15	2.53	176		
	N1—I3—I2 (neighboring chain)	~2.15	3.36	172		
$(I\cdot uro_2)I_3$	Uro—I—uro	2.30	2.30	177	II, A	
$(I(3\text{-}pic)_2)BF_4$	3-pic—I—pic-3	2.24	2.24	180	II, A	
$(I\cdot py_2)I_3\cdot 2I_2$	Py—I—py	2.16 ± 0.1	2.16 ± 0.1	180	II, A	
$(NI_3\cdot I_2\cdot uro)_n$	N1—I2—N4′	2.14	2.57	179	II, I	8
	N1—I1—N2	2.14	2.58	175		
	I4—I3—N1	2.81	2.47	175		
	I3—I4—N3	2.81	3.23	178		
$(HCONI_2)_n$	N—I2—O	2.10	2.56	171	II, J	9
	N—I1—O	2.04	3.12	151		

[a] Sum of van der Waals radii according to Pauling (*121*): N + I, 3.65; O + I, 3.55; I + I, 4.30 Å.

will also be bond angles of ca. 180° and ca. 90° with bonds of the 3 center–4 electron type. [This expectation has recently been fulfilled by *N*-chloro-3-aza-3*H*,2,1-benzoxiodol-1-yl chloride (III) (*112*).]

L. Behavior of Nitrogen Triiodide-3-ammonia in Solution, Especially in Liquid Ammonia

1. Nature of Species in Solution: Experimental Evidence for Occurrence of Monoiodamine-1-ammonia in Liquid Ammonia

Nitrogen triiodide-1-ammonia has a very low solubility in all solvents that have so far been studied. It is to be assumed or has been proven that this solubility depends on a reaction between iodine, acting as an acceptor, and the solvent, acting as a competing base:

$$NI_3 \cdot NH_3 + 3OH^- \overset{H_2O}{\rightleftharpoons} 2NH_3 + 3OI^- \quad (28) \qquad (5)$$

$$NI_3 \cdot NH_3 + 3ROH \overset{ROH}{\rightleftharpoons} 2NH_3 + 3ROI \quad (78) \qquad (6)$$

$$NI_3 \cdot NH_3 + 3R_2NH \overset{R_2NH}{\rightleftharpoons} 2NH_3 + 3R_2NI \quad \text{(Section II, G)} \qquad (7)$$

In liquid ammonia, nitrogen triiodide-1-ammonia is at once converted into nitrogen triiodide-3-ammonia, which is likewise poorly soluble in this solvent (ca. 1 mg/ml at −75°C). What species are present in the liquid ammonia solution?

Our working hypothesis is that, by analogy with Eqs. (5)–(7), a small amount of monoiodamine-1-ammonia, $H_2NI \cdot NH_3$, is formed in the equilibrium and that this has twofold coordinated iodine with a bond angle of ~180° [Eq. (8), vertical], as do the solid nitrogen–iodine compounds considered in Sections II, A–K.

So far this hypothesis lacks proof, but the following experimental findings are not inconsistent with it.

1. Solid nitrogen triiodide-3-ammonia is completely stable in an atmosphere of ammonia at −25°C, whereas it decomposes slowly under liquid ammonia even at −75°C. There must, therefore, be an unstable nitrogen–iodine compound in solution that is in equilibrium with nitrogen triiodide-3-ammonia (*91*).

2. The greater ease of decomposition of the dissolved compound may be explained by the free pair of electrons on the nitrogen atom of

$$\begin{tikzcd}[column sep=small]
\begin{array}{c}[H_3N{-}I{-}NH_3]^+ + NH_3 + NH_2^-\\ \text{colorless}\end{array} \arrow[r, phantom, "\rightleftharpoons"] & \begin{array}{c}[H_3N{-}I{-}\overline{N}H_2] + 2NH_3\\ \text{yellow in solution}\\ \text{red in solid state}\end{array} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left, "(\times 3)"] & \begin{array}{c}[H_2\overline{N}{-}I{-}\overline{N}H_2]^- + NH_4^+ + NH_3\\ \text{red}\end{array} \arrow[dddd, shift left, "(\times 3n)"] \\
 & \begin{array}{l}[H_3N{-}I{-}\overline{N}IH] +\\ {[H_3N{-}I{-}\overline{N}H_2]} + 8NH_3\end{array} \arrow[u, shift left, "(\div 3)"] \arrow[d, shift left] & \\
 & {[H_3N{-}I{-}\overline{N}I_2] + 10NH_3} \arrow[u, shift left] \arrow[d, shift left, "(\times n)"] & \\
 & \begin{array}{c}[NI_3 \cdot NH_3]_n + 10nNH_3\\ \text{brown}\end{array} \arrow[u, shift left, "(\div n)"] \arrow[d, shift left] & \\
 & \begin{array}{c}[NI_3 \cdot 3NH_3]_n + 8nNH_3\\ \text{green}\end{array} \arrow[u, shift left] \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left, "< -75^\circ C"] & \begin{array}{c}[NI_3 \cdot NH_2]_n^{n-} + nNH_4^+ + 9nNH_3\\ \text{black}\end{array} \arrow[uuuu, shift left, "(\div 3n)"] \\
 & \begin{array}{c}[NI_3 \cdot \sim 5NH_3]_n + 6nNH_3\\ \text{red}\end{array} \arrow[u, shift left, "> -75^\circ C"] & \\
\text{acidic} & \text{neutral} & \text{basic}
\end{tikzcd}$$

(8)

monoiodamine-1-ammonia, which makes it easier for iodine to be split off as iodide ion with simultaneous nitrogen evolution:

$$[H_3N\text{—}I\text{—}\bar{N}H_2] \underset{(\div 3)}{\overset{(\times 3)}{\rightleftharpoons}} 3I^- + 3NH_4^+ + NH_3 + N_2 \tag{9}$$

3. Suspensions of nitrogen triiodide-3-ammonia in liquid ammonia are able to add I and NH_2 groups to C═C double bonds as in halogenhydrin reactions (*80*) (Section II, L, 2).

4. By chilling saturated solutions of nitrogen triiodide-3-ammonia with liquid nitrogen, a red solid compound with an N:I ratio of 2:1, which is not identical with nitrogen triiodide-~5-ammonia, discussed in Section II, D, may be obtained. It is much more readily decomposed and has an intense IR band at 480 cm^{-1} in the N—I stretching region (*80, 55*).

Our working hypothesis further predicts that the dissolved monoiodamine-1-ammonia will give up a proton in a basic solution containing amide and be transformed into the monoiodamine ion $[H_2NINH_2]^-$ [Eq. (8), horizontal].

This hypothesis is also not inconsistent with the following experimental observations:

1. Addition of potassium or sodium amide to a suspension of nitrogen triiodide-3-ammonia in a molar ratio of $3K(Na)NH_2{:}1NI_3 \cdot 3NH_3$ yields a red-colored solution from which nitrogen triiodide-3-ammonia separates again on addition of acid (ammonium iodide). Addition of less amide leads to black salts of low solubility, which have been more fully investigated in the case of the silver compound (obtained in an analogous reaction). With excess amide, they go over to the red solutions (*92*).

2. The extremely ready decomposition of the dissolved red substance to iodide and nitrogen, even at −75°C, may be explained by the presence of two pairs of free electrons on the nitrogen atom of the monoiodamine ion:

$$[H_2\bar{N}\text{—}I\text{—}\bar{N}H_2]^- \underset{(\div 3)}{\overset{(\times 3)}{\rightleftharpoons}} 3I^- + 4NH_3 + N_2 \tag{10}$$

3. A polarographic reduction stage may be identified in basic solutions of the red compound, which does not appear in acid or neutral solutions [Eq. (8), horizontal] and disappears when the red compound decomposes (*109*).

According to our hypothesis, the small amount of monoiodamine-1-ammonia is transformed almost completely in acid solutions containing ammonium salts into the diammineiodonium ion, $[H_3N\text{—}I\text{—}NH_3]^+$

[Eq. (8), horizontal], the iodide of which is in equilibrium with the iodine ammines:

$$\begin{tikzcd}
I_2 + x\cdot NH_3 \arrow[r, shift left] & \begin{array}{c} I_2\cdot NH_3 + (x\text{-}1)NH_3 \\ \text{brown} \end{array} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left, "(\times 2)"] & \begin{array}{c} I_2\cdot 2NH_3 + (x\text{-}2)NH_3 \\ \text{brown} \end{array} \arrow[l, shift left] \arrow[d, shift left] \\
& \begin{array}{c} {[H_3N{-}I{-}NH_3]^+ + I_3^-} \\ \text{brown} \end{array} \arrow[u, shift left, "(\div 2)"] & {[H_3N{-}I{-}NH_3]^+ + I^-} \arrow[u, shift left]
\end{tikzcd} \qquad (11)$$

The correctness of this hypothesis is supported by many experiments:

1. Many iodonium salts stabilized by N-bases are known (*64*, *56*, *118*, *125*, *88*). Among the factors determining their relatively high stability is, in our view, the absence of free electron pairs on the nitrogen.

2. Nitrogen triiodide-3-ammonia with little ammonium iodide and a large excess of ammonium nitrate dissolves to give a colorless solution. After pumping off the ammonia at room temperature, there is a stable colorless residue that gives iodine with aqueous sulfuric acid (*79*).

3. Nitrogen triiodide-3-ammonia when treated with a large excess of ammonium iodide in liquid ammonia solution at room temperature dissolves to give a stable brown solution in which iodine may be detected after removing the solvent [Eqs. (8) and (11)]. Conversely, treating of solid iodine with ammonia gas gives the solid brown compounds diiodine-1- and -2-ammonia, whereas dissolution of iodine in a large excess of liquid ammonia yields only iodonium cations and iodide anions as shown by the polarogram. When this solution is concentrated the solubility product of nitrogen triiodide-3-ammonia is exceeded and ammonium ions may be detected polarographically [Eqs. (8) and (11)] (*79*, *109*).

4. Saturated solutions of nitrogen triiodide-3-ammonia, ammonium iodide, and ammonia in di-*n*-butyl ether at −40°C contain a second conducting species in addition to ammonium iodide, as shown by conductivity measurements (*122*).

2. *Reaction with Organic Compounds*

a. Reaction with Primary and Secondary Amines. In accordance with Eq. (7), nitrogen triiodide-1-ammonia reacts with a large number of primary and secondary amines the more readily as the amine becomes more basic. The reactions with methylamine, dimethylamine, and ethylenediamine have already been discussed in Sections II, F and G. Recently this has been extended to the reaction in aqueous solution at 0°C with tri-, tetra-, penta-, and hexamethylenediamine, and the corresponding tetraiododiamines have been prepared. They are all deep red in color and decompose very rapidly at 0°C, their temperature sensitivity increasing with the chain length (*146*).

b. Reaction with Organic Compounds Containing Acidic CH *Groups.* In carrying out reactions, iodine was dissolved in excess of liquid ammonia at −33°C. According to Eqs. (8) and (11) of Section II, L, 1, the resulting suspension contains solid nitrogen triiodide-3-ammonia. In solution, ammonium and iodide ions as well as an equilibrium between iodonium cations and iodoamine-1-ammonia are to be expected. This equilibrium should be shifted almost completely in favor of iodonium cations because of the presence of ammonium ions. The suspension thus appears to contain several species of active iodine. The mixture remaining after reaction with the organic compound was worked up in different ways. Table XVI shows recent results (*32*, *33*, *39*). They are classified according to the final product, since only in a few cases (reactions 14–16) was it possible to isolate or stabilize the primary product because of secondary reactions in liquid ammonia.

The following points seem to be of interest:

1. As the primary products of reactions 14–15 (Table XVI) are formed via substitution of one or more protons by iodonium cations, it is concluded that this is the primary step in all reactions of organic compounds with acidic C—H groups.

2. Reactions 9 and 16 are exceptions. The primary product of reaction 16 is explained by addition of iodonium and iodide ions to the phosphorus atom. Reaction 9 could also be explained by a two-center reaction of iodamine with the double bond as the primary step. This view of the mechanism is supported by the observation that diethyl fumarate does not react at all. How far this phenomenon depends on the cis or trans configuration at the double bond requires further consideration. Steric factors alone are probably not decisive, otherwise cumarin and ethyl *cis*-cinnamate would likewise undergo a two-center reaction. In fact, the latter does not react at all and cumarin does so only at the aromatic ring (reactions 8 and 10).

3. In reacting organic compounds with the nitrogen triiodide-3-ammonia suspension, one often finds two or more reaction products (compare reactions 1 and 15; 5, 11, and 12; and 8 and 10). The kind of reaction product often depends on the way in which the reaction material is worked up (reaction 15).

4. The suspension is not only an iodinating but also an aminating reagent.

TABLE XVI

REACTION OF NITROGEN TRIIODIDE-3-AMMONIA WITH C—H ACIDIC ORGANIC COMPOUNDS IN LIQUID AMMONIA AT −33°C

Reaction No.	Starting material	Molar ratio, organic compound:I^+	Yield (%)	Final product
		Final product only iodinated		
1	Diethyl malonate	1:2, 1:3	~20	Tri-, tetraiodomethane
2	Barbituric acid	1:1	80	Iodobarbituric acid
3	Methone	1:1	~100	Ammonium salt of 2-iodomethone
4	Acetone		good	Triiodomethane
5	Ethyl acetoacetate	1:2	~13	
6	Mesityl oxide	1:1	~25	
7	Phenol	1:1	60 Very low	*p*-Iodophenol Triiodophenol
8	Cumarin	1:1	40 Small	6-Iodocumarin 3,5-Diiodosalicylic aldehyde
		Final product iodinated and aminated		
9	Diethyl maleate	1:1	20	α-Amino, α′-iodomaleinimide
10	Cumarin	1:1	15 Very low	5-Iodocumaric amide 3,5-Diiodocumaric amide
11	Ethyl acetoacetate	1:2	4	Diiodoacetamide
		Final product only aminated		
12	Ethyl acetoacetate	1:2	25	Oxalamide
13	Diaminomalondiamide	1:1	66	

Reaction No.	Starting material	Molar ratio	Primary product	Yield (%)	Final product
14	Ethyl- (methyl) phenylacetate	1:1	Ethyl- (methyl-) α-iodophenylacetate	60–70	Phenyglycinamide
15	Diethylmalonate	1:2	Diethyldiiodomalonate	30 20	Diaminomalondiamide Ethyl carbamate
16	Triphenylphosphine	1:1	Triphenylphosphinediiodide	73	Triphenylphosphineiimide

5. Similar organic compounds give similar reactions (compare the iodoform in reactions 1, 4, 5, and 6).

6. A comparison shows that iodination reactions with dimethyliodamine also take place with a suspension of nitrogen triiodide-3-ammonia in liquid ammonia. Conversely, however, not all of the iodination reactions that can be carried out with this suspension will

occur with dimethyliodamine; for example, maleic ester (reaction 9) and cumarin (reactions 8 and 10) do not react with dimethyliodamine. This may be ascribed to the positive inductive effect ($+I$ effect) of the methyl groups on the nitrogen, which makes cleavage of the N—I bond in iodonium and amide ions more difficult.

III. Nitrogen Trichloride

There is a fundamental difference between the behavior of nitrogen–chlorine and nitrogen–iodine compounds. The greater covalent bond energy of the nitrogen–chlorine bond and the much smaller tendency of the chlorine to interact with a second nitrogen by a 3 center–4 electron bond or an oxygen (*12*) or chlorine atom implies nitrogen–chlorine compounds in general to be not polymeric and to be more soluble than nitrogen–iodine compounds.

A. STRUCTURE OF DISSOLVED AND GASEOUS NITROGEN TRICHLORIDE, NCl_3

The high solubility of nitrogen trichloride in many nonpolar solvents indicates a monomeric structure for this compound. Its molecular structure in solution has been elucidated simultaneously by several groups of workers using IR and Raman spectroscopy (*8, 15, 22, 69, 129*). The spectra (Table XVII) can be satisfactorily assigned on the assumption of a pyramidal structure with C_{3v} symmetry. (For force constant calculations, see Section III, C.) Electron diffraction investigations (*13*) and the microwave spectrum (*17, 16*) of the gaseous trichloride confirm the pyramidal structure (∢Cl—N—Cl, 107°; *r* N—Cl, 1.76 Å).

B. INFRARED SPECTRUM AND STRUCTURE OF SOLID NITROGEN TRICHLORIDE

The IR spectrum of solid nitrogen trichloride (*137*) (Table XVII) shows about the same stretching frequencies (ν_1, ν_3) as the dissolved compound. Of the two bending frequencies, the asymmetric (ν_4) is displaced from 258 to 230 cm^{-1}; the symmetrical bending frequency (ν_2) cannot be observed but its position may be calculated as 389 cm^{-1} from the observed combination band $\nu_2 + \nu_4$ at 619 cm^{-1}. The deviation of the bending frequencies from those of dissolved nitrogen trichloride may be attributed to the change to the solid state, which has a greater influence on the bending vibrations than on the stretching vibrations.

TABLE XVII

INFRARED AND RAMAN SPECTRA OF NITROGEN TRICHOLORIDE-^{14}N and -^{15}N IN THE RANGE OF FUNDAMENTAL VIBRATIONS[a]

IR spectra			Raman spectra		
$^{14}NCl_3(CCl_4)$ (cm^{-1})	$^{14}NCl_3$ (solid −185°C) (*137*) (cm^{-1})	$^{15}NCl_3(CCl_4)$ (cm^{-1})	$^{14}NCl_3(CCl_4)$ (cm^{-1})	$^{15}NCl_3(CCl_4)$ (cm^{-1})	Assignment
643 ss	642 ss	627 ss	643 w	628 w	ν_3 ν_{as} N—Cl
608 sh	619 sh				$\nu_2 + \nu_4$
520–540 w	542 m	510–530 w	541 s	528 s	ν_1 ν_s N—Cl
385 w		371 w			$\nu_3 - \nu_4$
349 w		349 w	349 ss	348 ss	ν_2 δ_s Cl—N—Cl
258 m	230 m	258 m	257 m	257 m	ν_4 δ_{as} Cl—N—Cl

[a] Intensities: ss, very strong; s, strong; sh, shoulder; m, medium; w, weak.

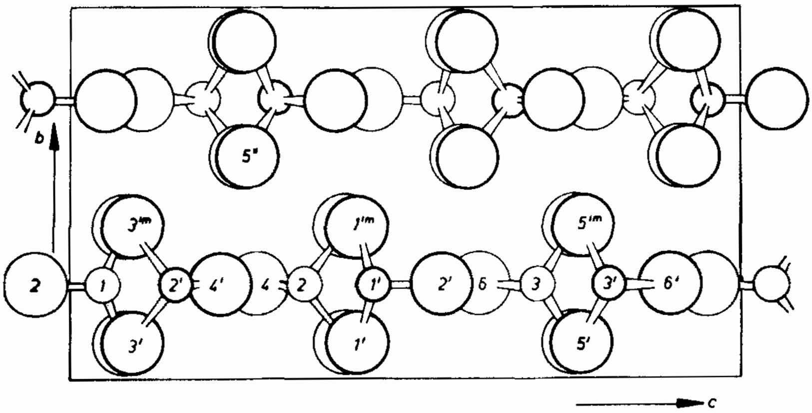


FIG. 10. Projection of the rhombic structure of nitrogen trichloride on the (100) plane. Molecules shown in heavy print lie at $x \sim 0.5$; the others are at $x \sim 0$ (*60*).

A further doubtful band observed at 155 cm^{-1} might be associated with weak intermolecular N···Cl interaction.

X-Ray structural analysis of solid nitrogen trichloride (*60*) (Figs. 10 and 11) shows a molecular lattice made up of nitrogen trichloride pyramids, which are stacked in layers at right angles to the *b*-axis (parallel to the *ac* plane). Pyramids within a layer are arranged with

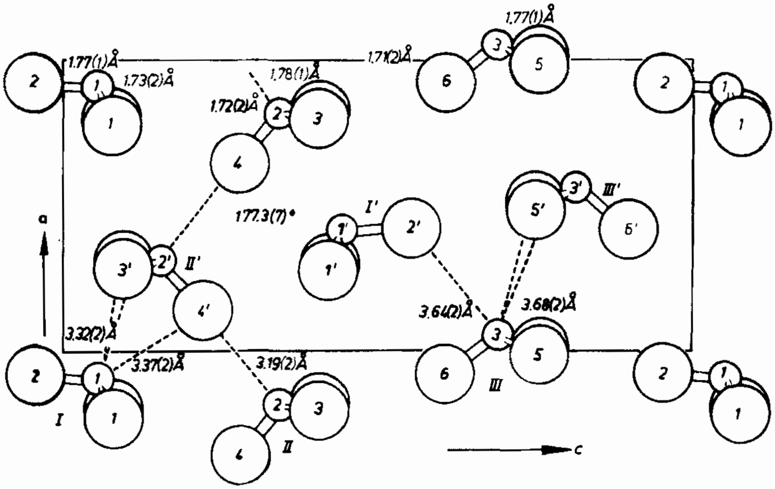


FIG. 11. Projection of the rhombic structure of nitrogen trichloride on the (010) plane. Only molecules with $y \sim 0.25$ are shown for the sake of clarity (molecules with $y \sim 0.75$ are omitted) (*60*).

the same orientation, whereas those in neighboring layers have an antiparallel orientation. The pyramids form undulating layers at right angles to the *a*-axis (parallel to the *bc* plane). Their projection on the *bc* plane shows that the chlorine atoms are approximately hexagonally close-packed.

The N—Cl bond distance and the Cl—N—Cl bond angle within a nitrogen trichloride pyramid vary appreciably, from 1.71 to 1.78 Å, with a weighted mean of 1.75 Å, and from 105.1 to 109.6° and, as a result of this, their ideal C_{3v} symmetry is lowered to m. The cause of this distortion is to be sought in generally very weak but varying intermolecular interactions. It is worth mentioning the distorted octahedral or trigonal prismatic coordination of the nitrogen atoms N1 and N3 (Fig. 11), although this will not be discussed further here since distances N1—Cl3′ (3.3), N1—Cl4′ (3.4), N3—Cl2′ (3.6), and N3—Cl5′ (3.7 Å) either reach or exceed the sum of the van der Waals radii of nitrogen and chlorine. Of greater significance in our context is the distance N2—Cl4′ (or N2′—Cl4) which, at 3.19 Å, is smaller than the sum of the van de Waals radii, and the angle N2—Cl4′—N2′ (or (N2′—Cl4—N2) which, at 177.4°, is practically 180°. As a consequence of this, part of the structure of nitrogen trichloride is made up of chains of NCl_4 tetrahedra parallel to the *a*-axis. These are formally similar to the chains of NI_4 tetrahedra discussed in Section II and with the linear twofold coordination of iodine which was stressed there. For nitrogen trichloride, the N—Cl···N grouping is, of course, unsymmetrical, and intermolecular nitrogen–chlorine interactions are very weak compared with those in nitrogen triiodide. Intermolecular chlorine–chlorine distances that are shorter than the sum of the van der Waals radii (3.60 Å) also occur. These are between the layers at right angles to the *b*-axis (parallel to the *ac* plane) (not shown in Fig. 10). These distances (3.37 and 3.42 Å) resemble the intermolecular distances found in solid chlorine (3.34 Å) (*18*), where they are interpreted as indicative of weak intermolecular interactions (*155*, *113*). The structure shows very many similarities to that of chloroform, except that there intermolecular interactions play no part (*35*, *18*, *94*, *60*).

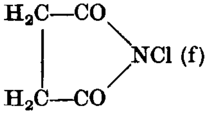
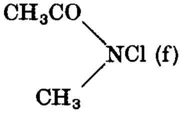
C. EXTENT OF VARIATIONS IN THE N—Cl BOND

In Table XVIII, results for nitrogen trichloride are compared with those for other nitrogen–chlorine compounds. Force constants cannot always be quoted without reservations since their calculation depends in part on estimated or extrapolated N—Cl distances.

The almost ideal tetrahedral angle in nitrogen trichloride and the

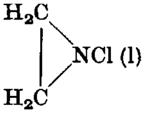
TABLE XVIII

BOND LENGTHS, FORCE CONSTANTS, AND IR WAVE NUMBERS FOR THE N—Cl BOND

Compound[a]	$r_{N—Cl}$ (Å; mean value m)	$f_{N—Cl}$ (mdyn/Å)	ν N—Cl (cm^{-1})	Refs.[b]
	With sp^3 hybridization at nitrogen			
$Ag[N(C_6H_{11})ClO_3]\cdot\frac{1}{2}H_2O$ (f)	1.63m		730	*126, 6*
F_2NCl (g)	1.73	3.13	697	
$HNCl_2$ (g)		2.93	687	
			666	
H_2NCl (g)		3.06	686	
CH_3NCl_2 (g)	1.74		667	
			656	
$[Pt(NH_3)_3(NCl_2)_2Cl]Cl$ (f)	1.75 m		664	*156, 157*
			644	
NCl_3 (g)	1.76		652	*13, 17*
(l)		2.72	643	
			541	
(f)	1.75 m		642	*60, 137*
			542	
$(CH_3)_2NCl$ (g)	1.77		600	
	With sp^2 hybridization at nitrogen			
K_2NClO_3 (f)	1.41	8.81	1267	*42*
$KHNClO_3$ (f)	1.64		865	*2*
NCl (l)		4.0	824	
N_3Cl (g)	1.745			*19*
(l)			724	
$F_2S(O)NCl$ (g)	1.72		670	*115*
F_2SNCl (g)	1.72		642	*54*
OCNCl (g)	1.70			
(f)		2.84	603	
	1.69		530	
OSNCl (g)	1.70	2.63	526	*114*
			483	
$[(CH_3)_3Si]_2NCl$ (f)			434	
O_2NCl (g)	1.83	2.46	370	
ONCl (g)	1.95	1.27	332	

(*continued*)

Table XVIII—*Continued*

Compound[a]	$r_{N—Cl}$ (Å; mean value m)	$f_{N—Cl}$ (mdyn/Å)	ν N—Cl (cm^{-1})	Refs.[b]
	With *sp* hybridization at nitrogen			
Cl_3VNCl (g)	1.60			*116*
(f)	1.59		500	*34*
	Without hybridization at nitrogen			
			563	

[a] Abbreviations: (g) gaseous; (fl) liquid; (l) in solution; (f) solid.

[b] References cited only where data are not given by Höhne *et al.* (*74*).

almost complete absence of intermolecular contacts in the solid state emphasize the correctness of the assumption that there is a relatively pure N—Cl single bond in this molecule. The experimental N—Cl stretching force constant of about 2.72 mdyn/Å accordingly represents that of a single N—Cl bond. In fact, comparable $f_{N—Cl}$ values are found for other nitrogen–chlorine compounds ($HNCl_2$, OCNCl, OSNCl) in which a single N—Cl bond may also be assumed. When Siebert's equation (*140*) is used in calculating the single bond force constant, using the correction factor of Goubeau (*51*) which takes account of mutual repulsion between the free electron pairs on nitrogen and chlorine, a quite similar value of 2.4 mdyn/Å is obtained.

The results in Table XVIII show the strong influence of charge effects on the N—Cl stretching force constant. In nitrosyl and nitryl chloride, for example, $f_{N—Cl}$ values are strikingly reduced, which can be explained by the participation of ionic structures. Moreover, other effects are also able to influence the N—Cl stretching force constant: The inductive effect of strongly electronegative substituents, for example, leads to an increase in $f_{N—Cl}$ (F_2NCl). An increase can also be brought about particularly by the double-bond effect, which is favored by the large total electronegativity and the small electronegativity difference for nitrogen and chlorine; it is also influenced by substituents on both elements (NCl, K_2NClO_3) (*51*, *74*).

Changes in the N—Cl stretching force constant (*F*-matrix) that have been discussed will also change the N—Cl wave number (λ) according to

$$G \cdot F - E \cdot \lambda = 0 \tag{12}$$

where G = G-matrix (masses, valence angle, internuclear distance), F = F-matrix (force constants, internuclear distance), E = unit matrix, and λ = wavelength (wave number). Thus, for example, in nitrosyl or nitryl chloride, there is a decrease in $\nu_{N—Cl}$ as a result of a decrease in $f_{N—Cl}$, whereas an increase in $f_{N—Cl}$, as for example in chlorodifluoramine, nitrogen monochloride, or potassium amidoperchlorate causes an increase in $\nu_{N—Cl}$ compared with the value for nitrogen trichloride.

The N—Cl wave number (λ) changes not only with the force constant (F-matrix), but also with the mass of the ligands bonded to nitrogen and chlorine and the effective angle made by the nitrogen–chlorine bond and these masses (G-matrix). Thus, for example, *N*-chlorosuccinic acid imide and *N*-chloro-*N*-methylacetamide show a lower wave number than compound OCNCl because two masses instead of one are directly bonded to sp^2-hybridized nitrogen. The wave number for compounds with sp^2 hybridization at nitrogen is displaced relative to that for compounds of about the same weight but sp^3 hybridization, by about 100 cm^{-1} toward higher wavelengths because the angle with which the masses operate at the nitrogen–chlorine bond increases from 109° to 120°.

The bond lengths shown in Table XVIII are all determined experimentally. The mean value of $r_{N—Cl}$ in nitrogen trichloride lies at 1.75 Å, which is close to $r_{N—Cl} \sim 1.7$ Å found for all compounds with an N—Cl single bond (OCNCl, OSNCl). The sum of the covalent radii (1.69 Å) (*121*) indicates too that a single bond requires a bond length of ca. 1.7 Å. Substantially shorter values of $r_{N—Cl}$ correspond with multiple bonding, whereas longer distances are indicative of an ionic component in the bond.

Reference may be made again to the expected inverse relationship between force constants and bond length. Overall, there is an astonishing range of variation in the N—Cl bond.

D. STRUCTURE OF SOLID TRIAMMINE BISDICHLORAMIDOCHLOROPLATINUM(IV) CHLORIDE, $[Pt(NH_3)_3(NCl_2)_2Cl]Cl$

It is evident from Table XVIII that replacement of a chlorine atom in nitrogen trichloride by platinum, i.e., the use of NCl_2 ligands in platinum complexes, does not have a substantial influence on structural relationships of the NCl_2X group (X = Cl, Pt). The N—Cl distances and hybridization at nitrogen remain unchanged on average, and the N—Cl wave number is also not altered. Figure 12 shows the structure of the $[Pt(NH_3)_3(NCl_2)_2Cl]^+$ cation elucidated by X-rays (*156, 157*), whereas

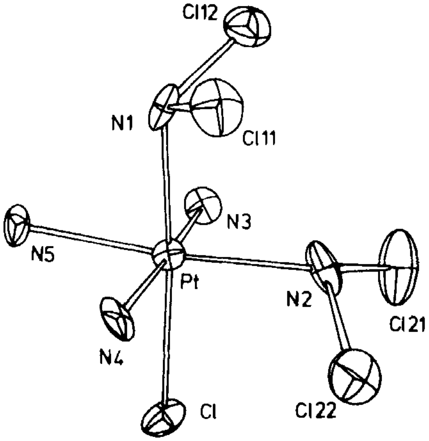


FIG. 12. Structure of the triammine bisdichloroamidochloroplatinum(IV) chloride cation (*156*).

Table XIX gives relevant bond distances and angles. The compound, which was originally prepared according to (*101*)

$$[Pt(NH_3)_5OH]Cl_3 + 4Cl_2 \longrightarrow [Pt(NH_3)_3(NCl_2)_2Cl]Cl + 5HCl + H_2O \quad (13)$$

has recently been obtained by the following reaction (*117*) as beautiful red crystals that are shock-sensitive:

$$[Pt(NH_3)_5Cl]Cl_3 + 4Cl_2 \longrightarrow [Pt(NH_3)_3(NCl_2)_2Cl]Cl + 6HCl \quad (14)$$

The reactions are interesting examples of the extensive current studies on the reactivity of ligands in transition metal complexes (*143*).

TABLE XIX

DISTANCES AND ANGLES IN CATION $[Pt(NH_3)_3(NCl_2)_2Cl]^+$

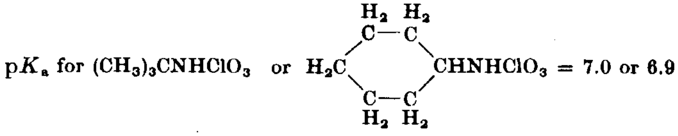
Pt—N1	2.07 Å	Pt—N1—Cl11	108.6°
Pt—N2	2.10 Å	Pt—N1—Cl12	111.0°
Pt—N3	2.04 Å	Cl11—N1—Cl12	102.6°
Pt—N4	2.02 Å	Pt—N2—Cl21	111.3°
Pt—N5	2.12 Å	Pt—N2—Cl22	114.0°
Pt—Cl	2.35 Å	Cl21—N2—Cl22	109.1°
N1—Cl11	1.82 Å		
N1—Cl12	1.77 Å		
N2—Cl21	1.75 Å		
N2—Cl22	1.66 Å		

E. *N*-PERCHLORYL COMPOUNDS

Table XVIII gives three examples showing the wide variation in *N*-perchloryl compounds. This first came to light after the recent preparation of a large number of organic *N*-perchloryl compounds by reaction of amines with the new perchlorylating reagent, dichlorine heptoxide (*6*, *10*),

$$2R_1R_2NH + Cl_2O_7 \xrightarrow[25^\circ \text{ to } -20^\circ C]{CCl_4} R_1R_2NClO_3 + R_1R_2NH_2^+ClO_4^- \qquad (15)$$

where R_1 = organic group and R_2 = organic group or hydrogen. The resulting colorless or, at the most, faintly yellow compounds (oils) are not isolated as a rule because of their explosive nature but are identified in carbon tetrachloride solution by ratio analysis as well as by IR and ^1H NMR spectroscopy. When they still have hydrogen bonded to nitrogen, they are appreciably acidic:



$$pK_a \text{ for } (CH_3)_3CNHClO_3 \text{ or } H_2C\begin{array}{c}\overset{H_2\;H_2}{C{-}C}\\ \\ \underset{H_2\;H_2}{C{-}C}\end{array}CHNHClO_3 = 7.0 \text{ or } 6.9$$

compared with pK_a for $1(H_2NClO_3)$ or $2(H_2NClO_3)$ which is 5.5 or 11.9, respectively. More stable solid potassium and silver salts may be made which can be identified by element analysis and their IR spectra. Table XX shows the new *N*-perchloryl compounds with some of the older ones for comparison.

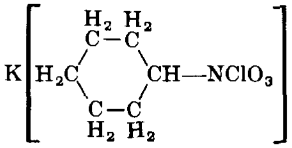
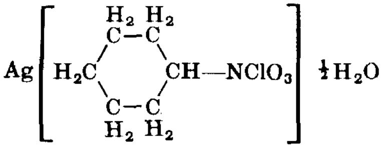
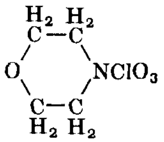
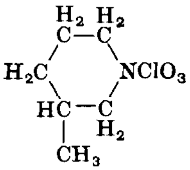
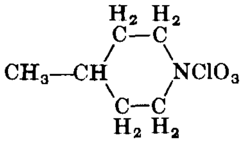
Table XX also shows the most important IR stretching frequencies of these compounds and their assignments so far as thay may be obtained by comparison with assignments for the spectra of the ions and compounds $NClO_3^{2-}$ (*93*, *52*), $HNClO_3^-$ (*93*), $ROClO_3$, $HOClO_3$, $XOClO_3$ (X = halogen), and $O_3ClOClO_3$ (*128*, *135*, *134*). Splitting of the ν_{as} O—Cl frequencies in some *N*-perchloryl compounds can be attributed to lowering of the C_{3v} symmetry of the $NClO_3^-$ ion to C_s (*119*), whereas the partial doubling of the ν_s Cl—O frequencies in the cyclic *N*-perchloryl compounds may be explained by equatorial and axial positioning of the ClO_3 group in relation to the organic ring.

Once it is realized that, because of the mutual coupling of ν_{N-Cl} and ν_s O—Cl, identification of these frequencies is not straightforward and that they can also be influenced by differing mass effects, then it can be established that in the series in Table XX, going from top to bottom

$$(K_2NClO_3{-}Ag_2NClO_3{-}KRNClO_3{-}KHNClO_3{-}AgRNClO_3{-}R_2NClO_3{-}RHNClO_3),$$

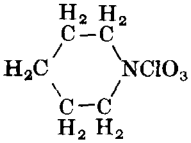
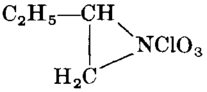
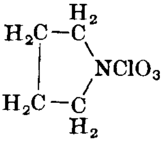
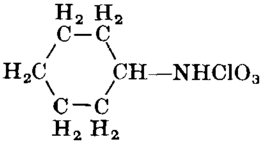
TABLE XX

THE MOST IMPORTANT STRETCHING FREQUENCIES OF THE NEWER *N*-PERCHLORYL COMPOUNDS (WITH OLDER VALUES FOR COMPARISON)

Compound	ν N—Cl (cm^{-1})	ν_s O—Cl (cm^{-1})	ν_{as} O—Cl (cm^{-1})	Refs.
K_2NClO_3	1264	815	890	*26, 105, 93, 52*
Ag_2NClO_3	1021 973	848	944	*93*
	940	~1000	1120 1081	*6*
$K[(CH_3)_3CNClO_3]$	937	1020	1080	*6*
$KHNClO_3$	865	988	1121	*93*
	730	951	1136	*6*
	695	1005 974	1240 1202	*6*
	680	1000 955	1210 1180	*6*
	680	1010 960	1215 1185	*6*

(continued)

Table XX—*Continued*

Compound	ν N—Cl (cm^{-1})	ν_s O—Cl (cm^{-1})	ν_{as} O—Cl (cm^{-1})	Refs.
	680	1040 990	1225 1190	*37, 6, 10*
$(C_5H_{11})_2NClO_3$	680	1020	1240 1200	*10*
	680	1020	1245 1210	*10*
$(C_2H_5)_2NClO_3$	670	995	1220 1185	*6, 10*
$(C_3H_7)_2NClO_3$	665	1005	1230 1195	*6*
$(C_4H_9)_2NClO_3$	660	1000	1220 1185	*6*
$(CH_3)_2NClO_3$	655	1000	1220 1190	*6*
	640	1005	1215 1175	*6*
$CH_3—(CH_2)_5—NHClO_3$	665	1020	1240 1210	*10*
$(CH_3)_2CH—NHClO_3$	660	1020	1230 1205	*10*
$CH_3—(CH_2)_3—NHClO_3$	655	1010	1230 1200	*6, 10*
	654	1009	1204	*6*
$(CH_3)_3C—NHClO_3$	647	1012	1254 1198	*6, 10*
$CH_3—(CH_2)_2—NHClO_3$	645	1030	1250 1210	*10*

ν_{N-Cl} decreases from ~1260 to 650 cm^{-1} and ν_{as} O—Cl rises from ~900 to ~1250 cm^{-1}, corresponding to a decrease in the double-bond character of the N—Cl bond and to an increase for the O—Cl bond. The decrease in double-bond character for the N—Cl bond is to be associated with increase in the electronegativity of nitrogen with change in the atom attached to it: It attracts the π-bonding electron pair of the N—Cl double bond increasingly to nitrogen. The resulting increasing electron requirement of chlorine is then satisfied in increasing measure by π electrons from oxygen, which will explain the increase in the double-bond character of the O—Cl bond. A corresponding effect has already been observed and described in a comparison of the IR spectra of $NClO_3^{2-}$ and $FClO_3$ (*52*).

X-Ray structural analysis of potassium amidoperchlorate (*42*), potassium hydrogen amidoperchlorate (*2*), and silver cyclohexylamidoperchlorate·$\frac{1}{2}H_2O$ (*126*) confirm this interpretation from interatomic distances (Table XXI). The small value of r_{N-Cl} in the amidoperchlorate anion (in which there are three pairs of electrons available for π bonding and a low electronegativity at nitrogen) contrasts with the significantly greater value of r_{N-Cl} (which is close to that for a single bond) in potassium hydrogen amidoperchlorate and silver cyclohexylamidoperchlorate (with no free electron pair, but with two silver ligands, distorted sp^3 hybridization, and a higher electronegativity at nitrogen). Conversely, Cl—O distances decrease progressively in the series K_2NClO_3—$KHNClO_3$—$AgN(C_6H_{11})ClO_3\cdot\frac{1}{2}H_2O$.

TABLE XXI

DISTANCES AND ANGLES IN POTASSIUM AMIDOPERCHLORATE (K_2NClO_3), POTASSIUM HYDROGEN AMIDOPERCHLORATE ($KHNClO_3$), AND SILVER CYCLOHEXYLAMIDOPERCHLORATE–WATER [$AgN(C_6H_{11})ClO_3\cdot\frac{1}{2}H_2O$]

Distance and angle measured	$AgN(C_6H_{11})ClO_3\cdot\frac{1}{2}H_2O$	$KHNClO_3$	K_2NClO_3
O—Cl	1.38–1.44 Å	1.43–1.46 Å	1.50–1.52 Å
N—Cl	1.61–1.65 Å	1.64 Å	1.41 Å
O—Cl—O N—Cl—O	104°–113°		109°
N—C	1.52–1.53 Å		
N—Ag	2.16–2.27 Å		
Cl—N—C	110°–112°		
Cl—N—Ag	107°–110°		
C—N—Ag	115°–121°		
Ag—N—Ag	87°–92°		

F. KINETICS OF FORMATION OF NITROGEN TRICHLORIDE IN SOLUTION

When ammonia is chlorinated with *t*-butyl hypochlorite the changes in concentration with time shown in Fig. 13 (*11*) may be observed by extinction coefficient measurements at the UV absorption maxima for the reagents (ammonia, *t*-butyl hypochlorite) and products (monochloramine, dichloramine, and nitrogen trichloride). A reaction scheme is then developed, on the basis of which concentration time curves may be calculated that are almost completely superposable on the experimental curves in Fig. 13. The scheme includes the basic steps

$$NH_3 + (CH_3)_3COCl \longrightarrow H_2NCl + (CH_3)_3COH \quad (16)$$

$$H_2NCl + (CH_3)_3COCl \longrightarrow HNCl_2 + (CH_3)_3COH \quad (17)$$

$$HNCl_2 + (CH_3)_3COCl \longrightarrow NCl_3 + (CH_3)_3COH \quad (18)$$

as well as two indispensable reactions,

$$H_2NCl + NCl_3 \longrightarrow 2HNCl_2 \quad (19)$$

$$NH_3 + HNCl_2 \longrightarrow 2H_2NCl \quad (20)$$

Only by Eq. (19) is it possible to explain why the nitrogen trichloride concentration remains small and the dichloramine concentration

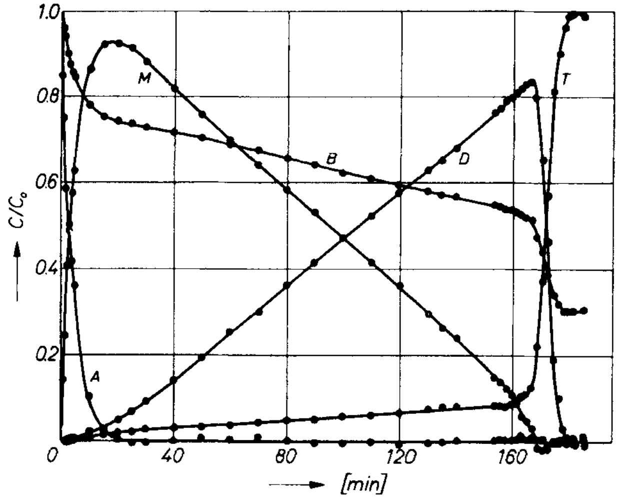


FIG. 13. Change in concentration with time for various substances in the reaction of 3.8 mmoles/liter ammonia with 15.4 mmoles/liter *t*-butyl hypochlorite in a mixed solvent containing cyclohexane and *t*-butanol (200 mmoles/liter) at 20°C. A = NH_3, B = $(CH_3)_3COCl$, M = H_2NCl, D = $HNCl_2$, and T = NCl_3. For A, M, D, and T the ratio C/C_0 denotes the ratio of the concentration at a given time to the initial concentration of A (or in the case of B, the initial concentration of B) (*11*).

increases simultaneously to over 80%, although the rate of formation of nitrogen trichloride is very large in comparison with the rate for dichloramine. The same is true for Eq. (20). The autocatalytic nature of the reaction leading to nitrogen trichloride when all the monochloramine has been used up is explained by

$$HNCl_2 + NCl_3 + (CH_3)_3COCl \longrightarrow 2NCl_3 + (CH_3)_3COH \tag{21}$$

Finally, the two reactions,

$$(CH_3)_3COCl \longrightarrow Cl\cdot + (CH_3)_3CO\cdot \tag{22}$$

$$NH_2Cl + 2Cl\cdot \longrightarrow NCl_3(d) + 2H\cdot \tag{23}$$

are necessary to explain the slow increase in nitrogen trichloride concentration in presence of monochloramine; it involves the mechanism for forming a deactivated nitrogen trichloride molecule [$NCl_3(d)$] that can no longer react with monochloramine according to Eq. (19).

For the kinetics of the thermal decomposition of nitrogen trichloride in chlorobenzene, see Ref. *127*.

IV. Nitrogen Tribromide

When the structures of solid polymeric nitrogen triiodide-1-ammonia and of solid nonpolymeric nitrogen trichloride are known, it is interesting to discover how solid nitrogen tribromide is constituted. Does the bromine of a nitrogen–bromine bond also form a contact with a second nitrogen (3 center–4 electron bond) or bromine atom? From all that is so far known about nitrogen–bromine compounds (*78*), it seems that the nitrogen–bromine bond occupies an intermediate position between an N—I bond, which readily forms such contacts, and an N—Cl bond, which does not do so.

It was first necessary to obtain a reproducible method for preparing nitrogen tribromide in solution and/or in the free state, for, unlike mono- and dibromamine, it is so far hardly known (*78*).

A. SYNTHETIC ROUTES TO NITROGEN TRIBROMIDE

Nitrogen tribromide was first observed as a product of the reaction of an acidic aqueous ammonia salt solution (pH = 4) with bromine and was characterized by determination of the nitrogen:bromine ratio and by UV spectroscopic methods (*36*, *144*, *78*). It was possible to isolate for the first time a solid containing nitrogen tribromide from these water or water–methanol solutions by extraction with ether and subsequent precipitation in Freon 12 at −110°C (*144*).

In the course of further attempts to prepare the pure tribromide (*96*, *83*) several possible ways were found for brominating ammonia directly. In dichloromethane at −87°C, it is possible to use bromine, bromine chloride, *N*-bromsuccinimide, dibromisocyanuric acid (DBI) (*44*), acetyl hypobromite, and *t*-butyl hypobromite as brominating agents. Bromination experiments with a polymeric brominating agent [*N*-brominated divinyl benzene–styrene–vinyl pyrrolidone copolymer (*68*); see also Ref. *106*] were unsuccessful. Addition of 20% acetone is necessary in the case of DBI to bring the reagent into solution and thus enable it to exert its brominating effect. Solid nitrogen tribromide, which is precipitated, is contaminated with various secondary products. Dissolution of the tribromide from the orange-red mixture with dichloromethane gave pure orange-yellow solutions (nitrogen: bromine ratio, 1:3); they are, however, of little use for preparative or spectroscopic investigations since nitrogen tribromide concentrations are about 4 × 10^{-3} moles/liter.

Pure solid nitrogen tribromide may be obtained in a reaction analogous to that used for *N*-iodamines (*139*, *146*) from bistrimethylsilylbromamine (*152*) and bromine chloride:

$$[(CH_3)_3Si]_2NBr + 2BrCl \xrightarrow[-87^\circ C]{\text{pentane}} NBr_3\downarrow + 2(CH_3)_3SiCl \qquad (24)$$

The deep red substance (nitrogen: bromine ratio, 1:3) is very temperature-sensitive and explodes even at −100°C in a Nujol–pentane suspension (1:2.7) on the least mechanical disturbance. Nitrogen tribromide is soluble without decomposition at low temperatures (< −80°C) in polar solvents that do not undergo bromination or oxidation.

B. Reactions and Spectra of Nitrogen Tribromide; Nitrogen Dibromide Monoiodide, NBr_2I

Nitrogen tribromide reacts instantly with ammonia to give dark violet monobromamine (*87*):

$$NBr_3 + 2NH_3 \xrightarrow[-87^\circ C]{CH_2Cl_2} 3NH_2Br\downarrow \qquad (25)$$

With tertiary N bases such as pyridine and urotropine, the bromine adducts of the bases are formed directly. In this, nitrogen tribromide differs from nitrogen triiodide-1-ammonia; the latter with tertiary bases first gives the nitrogen triiodide adducts, and the iodine adducts are formed from these in a subsequent reaction (Section II, E).

Methylene chloride solutions of iodine react with nitrogen tribromide in the same solvent to give solid red-brown nitrogen dibromide iodide (nitrogen:bromine:iodine ratio, 1:2:1), which is stable up to −20°C:

$$NBr_3 + I_2 \xrightarrow[-87°C]{CH_2Cl_2} NBr_2I\downarrow + IBr \qquad (26)$$

Solutions of nitrogen tribromide in the polar solvents studied are not suitable for IR and Raman spectroscopy because of numerous solvent bands. Since, on the other hand, pure solid nitrogen tribromide is difficult to handle (see above), the less explosive orange-red mixtures of solid nitrogen tribromide and ammonium bromide or acetate were finally examined (*96*, *83*). The band-rich spectra—the IR spectrum described earlier (*144*, *78*) requires some correction—rule out the assignment of C_{3v} symmetry to the monomeric NBr_3 molecule and bring up the question of intermolecular contacts. Further spectroscopic investigations should clarify which structural principle is operative in solid nitrogen tribromide. The ultraviolet spectra of nitrogen tribromide solutions have been known for some time (*36*, *144*, *78*).

C. INFRARED AND FURTHER STRUCTURAL STUDIES ON NITROGEN–BROMINE COMPOUNDS

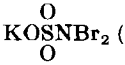
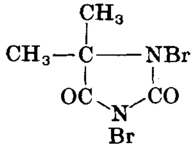
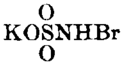
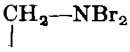
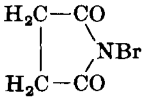
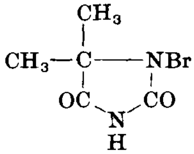
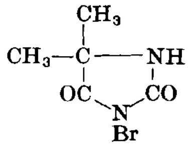
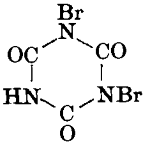
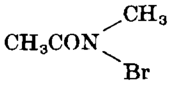
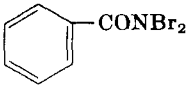
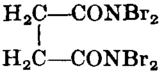
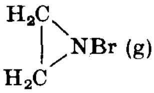
Hitherto there has been only scanty information on the position of N—Br stretching frequencies. A whole range of N—Br compounds has been measured down to 250 cm^{-1} (Table XXII), but often no assignments are given or the assignment given is regarded as uncertain. The most reliable are those where assignments for the corresponding N—Cl and N—I compounds are also considered, so that there is a possibility of making comparisons. The N—Br frequencies are then always found to lie between those of the N—Cl and N—I compounds (*73*, *136*). Some N—Br frequencies that have been assigned with some measure of certainty are 691 cm^{-1} [nitrogen monobromide in a matrix (*108*)], 560 and 470 cm^{-1} [solid nitrogen tribromide (*96*)], 540 cm^{-1} [dissolved monobromamine (*73*)], 451 cm^{-1} [liquid *N*-bromsulfinylimine (*31*)], and 265 cm^{-1} [gaseous nitrosyl bromide (*14*, *104*, *102*)].

The N—Br stretching force constants have been calculated on the basis of these assignments as 3.35 (nitrogen monobromide), 2.46 (*N*-bromsulfinylimine), and 1.13 mdyn/Å (nitrosyl bromide). As a rule they cannot be supported by measured N—Br distances.

The only N—Br distance measured by X-ray analysis is 1.82 Å in solid *N*-bromacetamide (*24*). This is close to the sum of the single covalent bond radii [$r_N = 0.70$, $r_{Br} = 1.14$ Å; $\Sigma\, r_{N+Br} = 1.84$ Å (*121*)]. Microwave spectra and electron diffraction investigations on gaseous

TABLE XXII

NITROGEN–BROMINE COMPOUNDS THE IR SPECTRUM OF WHICH HAVE BEEN MEASURED TO 250 CM⁻¹

Compound[a]	References	Compound[a]	References
With sp^3 hybridization at nitrogen			
 $\mathrm{KO\overset{O}{\underset{O}{S}}NBr_2}$ (f)	*136*	 (f)	*136*
 $\mathrm{KO\overset{O}{\underset{O}{S}}NHBr}$ (f)	*136*		
CH_3NBr_2 (l)	*47*		
 $\begin{array}{l}CH_2—NBr_2\\ \vert\\ CH_2—NBr_2\end{array}$ (f)	*48*	 (f)	*73*
CH_3NHBr (l)	*66*		
$(CH_3)_3CNBr_2$ (l)	*48*		
NBr_3 (f)	*96*	 (f)	*136*
H_2NBr (f)	*30*		
(l)	*73*		
$(CH_3)_2NBr$ (g)	*73*	F_2SNBr (fl)	*40*
(l)	*66*		
With sp^2 hybridization at nitrogen			
NBr (g)	*108*	 (f)	*136*
N_3Br (g)	*108*	OSNBr (fl)	*149, 31*
 (f)	*76*	$C_2H_5OCONBr_2$ (fl)	*136*
$HCONBr_2$ (f)	*47*	 (f)	*73*
CH_3CONBr_2 (f)	*47*	$HCl_2CCONBr_2$ (f)	*47*
OCNBr (f)	*43, 46*		
$CH_3CONHBr$ (f)	*24, 73, 154*	 (f)	*47*
CH_3CONBr_2 (f)	*136*		
$C_2H_5CONHBr$ (f)	*136*	ONBr (g)	*150, 95, 14,* *104, 102*
 $\begin{array}{l}H_2C—CONBr_2\\ \vert\\ H_2C—CONBr_2\end{array}$ (f)	*47*	(f)	*71, 102*
$C_2H_5CONBr_2$ (f)	*136*	Without hybridization at nitrogen	
BrNSNBr (f)	*138*		
$CClH_2CONBr_2$ (f)	*47*	 (g)	*132*
$(C_2H_5O)_2CNBr$ (f)	*136*		

[a] Abbreviations: (g) gaseous; (fl) liquid; (l) solution; (f) solid.

nitrosyl bromide are in agreement in giving an N—Br distance of 2.14 Å (*95, 150*). This long distance, which is supported by a low stretching frequency and a small force constant, is explained in terms of participation of an ionic limiting structure.

Potential energy curves have been calculated for the $^1\Sigma^+$ and the $^3\Sigma^-$ states of nitrogen monobromide (*75*). For a calculation of the dissociation energy of the N—Br bond in nitrogen monobromide, see Ram *et al.* (*130*), and for measurements of the heat of decomposition of bromine azide, see Dupre *et al.* (*25*). Thermodynamic functions have been calculated from spectroscopic data for compound F_2SNBr (*131*).

D. NITROGEN–BROMINE COMPOUNDS IN SOLUTION

1. *Solutions of Bromine in Liquid Ammonia*

Dilute solutions of bromine in liquid ammonia do not contain monobromamine at lower temperatures. This may be concluded from the absence of protons (ammonium ions) which would be formed in the reaction (*70*),

$$Br_2 + 2NH_3 \rightleftharpoons H_2NBr + NH_4^+ + Br^- \qquad (27)$$

The solvated bromine cation clearly has a sufficiently high stability in these solutions. In concentrated solutions, on the other hand, monobromamine and ammonium bromide are formed according to Eq. (27) (*86*).

2. *New Synthetic Routes to Organic Nitrogen–Bromine Compounds*

Although new preparative methods have been developed in recent years for organic nitrogen–chlorine and nitrogen–iodine compounds (e.g., Sections II, J and II, L, 2, a), the main emphasis in recent synthetic work has been on nitrogen–bromine compounds. The sudden increasing use of nitrogen–bromine compounds, especially *N*-bromosulfono- and carboxylic acid amides, as selective brominating agents or cyclization reagents (aziridine) and, therefore, as adjuncts in metallurgy, photography, agriculture, the textile industry, pharmacy, and the perfumery industry makes this understandable.

Thus alkyl compounds with —$CONBr_2$ and $>CNBr_2$ groups may be obtained in good yields at room temperature from the corresponding amides or amines and dibromisocyanuric acid in aprotic solvents (*45*, *47*, *48*). The synthesis of a crystalline monobromamine, *N*-brom-*t*-butylamine, by this route was also successfully carried out. Monobrominated alkyl compounds with the —CONHBr group may be obtained by the same method using less dibromisocyanuric acid (*50*). On the other hand, they were obtained in very good yield by reaction of the amide with sodium hypobromite and subsequent protolysis of —CONNaBr with dilute sulfuric acid in the presence of methylene chloride to extract the desired product (*3*).

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