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Some problems in the stereochemistry of nitrogen compounds in the gas phase

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ABTRACT. Data on the geometry of free molecules containing a nitrogen atom have been reviewed. Most attention has been paid to compounds of amines with a nitrogen–metal bond, nitro-compounds, and complex compounds. The applicability of various ideas on the relationship between the electronic structure and geometry of molecules has been analysed.

The bibliography contains 193 references.

Contents

I. Introduction 1169
II. Amino-derivatives 1169
III. Imino-, carbodi-imido-, and azino-derivatives 1175
IV. Nitro-compounds 1176
V. Complex compounds of nitrogen 1184
VI. Summary 1190

I. Introduction

The stereochemistry of nitrogen compounds is rich in different forms of valence state of the nitrogen atom and different types of bond between nitrogen and other elements. A large number of publications[1–8] have been devoted to the systematisation of data on the geometry of molecules in the gas phase and the discovery of structural regularities. The present review is restricted to a few classes of nitrogen compound, and most of the data systematised are not in the works cited above.

The analysis was based on two sections of Landolt–Bornstein[9] containing the results of electron diffraction (GE) and microwave (MW) studies of the structure of molecules in the gas phase up to and including 1985, and original publications for the following year. For the values of the parameters given in the text, the following dimensions are used: bond lengths in Ångstrom units (Å) and valence and dihedral angles in degrees (°). Their experimental errors in the last significant figures are given in brackets.

Since different methods of studying the structure were used, the geometric parameters, in particular the bond lengths, have slightly different physical significance, because of the slight (generally up to ~0.01 Å) influence of vibrational corrections (see for example Ref. 2).

II. Amino-derivatives

1. Amines with hydrocarbon substituents and halogenoamines

In the examination of the structure of amines, particular attention is usually paid to the geometry of the amine fragment, that is to the configuration of the bonds formed by the nitrogen atom and the lengths of the "nitrogen–substituent" bonds.

Table 1. Geometric parameters of alkylamine molecules.

Compound	N–C, Å	C–N–C, °	Method,* type of parameter	Refs.
CH_3NH_2	1.472(3)	–	GE+MW, r_g	[10]
$(CH_3)_2NH$	1.455(6)	111.8(8)	GE, r_a	[11]
	1.462(7)	112.2(5)	MW, r_s	[12]
$(CH_3)_3N$	1.458(4)	110.9(6)	GE, r_α	[13]
$(CF_3)_3N$	1.426(6)	117.9(4)	GE, r_0^δ	[14]
$C_2H_5NH_2$	1.470(10) *trans*	–	GE+RC+NC, r_g	[15]
	1.475(10) *gauche*			
$(CH_3)_3CNH_2$	1.493(6)	–	GE, r_g	[16]
$CH_2CH_2CHNH_2$	1.452(7)	–	MW, r_s	[17]
$(CH_3)_2NC_2H_5$	1.452(6)	111.3(10)	GE, r_a	[18]
$CH_2N(CH_3)_2]_2$	1.449(4)	110.7(10)	GE, r_α	[19]
$[(CH_3)_2CH]_2NH$	1.470(4)	120.1(10)	GE+VS+MM, r_g	[20]
$[(CH_3)_3C]_2NH$	1.467(15)	135(3)	GE, r_a	[21]
$(CH_3)_3CNHCH_2CH_3$	1.476(1) (C′)	117.6(11)	GE+VS+NC, r_g	[22]
	1.465(1)			
$(CF_3CF_2CF_2)_3N$	1.459(8)	120.0(2)	GE, r_g	[23]

*Notation: GE = gas-phase electron diffraction, MW = microwave spectroscopy, RC = rotational constants, NC = non-empirical calculations, VS = vibrational spectroscopy, MM = molecular mechanics.

The geometric parameters of a number of alkylamines are given in Table 1. The bonds formed by the nitrogen atom in ammonia and methylamines have a pyramidal configuration. The replacement of the hydrogen atoms in NH_3 by CH_3 groups increases the average valence angle α_N by ~3°:

Amine	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
$\bar{\alpha}_N$, °	106.7	110	108.6	110.9

In the methylamine series the N–C bond length tends to decrease on going from the primary to the tertiary amine. This trend is also observed in a series of alkylamines with heavier substituents, such as $C_2H_5NH_2$ [N–C 1.472(10) Å] and $C_2H_5N(CH_3)_2$ [N–C 1.452(6) Å].

On going from CH_3NH_2 to $C_2H_5NH_2$ the N–C bond length remains unchanged, but the presence of the bulky t-butyl substituent in $(CH_3)_3CNH_2$ increases the N–C bond length to 1.493(6) Å.

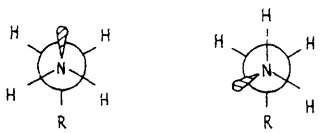
Replacing the electron-donor CH_3 groups in the trimethylamine molecule by the electron-acceptor CF_3 groups leads to flattening of the configuration of the nitrogen atom [the CNC angle is 117.9(4)°]. At the same time the N–C bonds are shorter [1.426(6) Å] than those in methylamines.

On going from $(CF_3)_3N$ to $(CF_3CF_2CF_2)_3N$ the configuration of the bonds formed by the nitrogen atom becomes completely planar, with a CNC angle of 120.0(2)°, and the N–C bond length increases by ~0.03 Å.

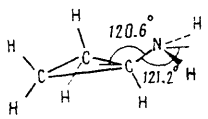
The steric interactions between the t-butyl groups in the $HN[C(CH_3)_3]_2$ molecule increase the CNC angle to 135(3)° compared with the corresponding angle [120.1(10)°] in $NH[CH(CH_3)_2]_2$, indicating that the steric repulsion of the t-butyl groups is greater than that of the isopropyl groups.

Thus the configuration of the bonds formed by the amine nitrogen atom in alkylamines depends on the type of substituent and on steric factors.

In the study of the structure of more complex aliphatic amines such as $CH_3CH_2NH_2$, $CH_2CH_2CHNH_2$, $(CH_3)_2CHNH_2$,[24] $(CH_3)_2NC_2H_5$, $NH[C(CH_3)_3]_2$, $NH[CH(CH_3)_2]_2$, and $CH_2[N(CH_3)_2]_2$, the conformations of the molecules, in particular the rotational isomerism about the N–C bond, is also examined in detail. It has been shown, for example, that ethylamine consists of a mixture of *gauche*- and *trans*-isomers (~1:1) and that $\Delta H(gauche-\text{trans}) = 306(200)$ cal mol^{-1}.



In cyclopropylamine the amino-group is in the staggered "perpendicular" conformation relative to the cyclopropane ring†.



The conformations of the molecules of secondary amines are characterised by the two angles of rotation about the N–C bonds. For the $NH[CH(CH_3)_2]_2$ molecule these angles are the same and equal to 52(4)°, whereas in $NH[C(CH_3)_3]_2$ the t-butyl groups are rotated slightly differently (19° and 30°) relative to the N–C bond, and the axes of symmetry of these groups deviate from the direction of the N–C bonds by 2.5 ± 1.5°.

†According to the definition given by the authors cited, the term "perpendicular" conformation indicates that the lone pair of electrons of the nitrogen atom is situated above the three-membered ring and is projected on to the bisector of the CCC angle.

The geometric parameters of a number of halogenoamines are given in Table 2. A distinguishing feature of halogenoamines compared with ammonia and methylamines is the decrease in the valence angles XNX and XNY, and hence in the average valence angle at the nitrogen atom.

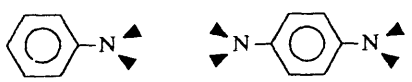
Table 2. Geometric parameters of halogenoamine molecules.

Compound	Bond lengths, Å		Valance angles, °		Method,* type of parameter	Refs.
NF_3	N—F	1.365(2)	FNF	102.4(3)	MW, r_e	[25]
NH_2F	N—F	1.400(2)	FNH	99.8(2)	ME, r_s	[26]
	N—H	1.026(2)	HNH	102.9(2)		
NF_2Cl	N—F	1.382(9)	FNF	103(1)	GE, r_a	[27]
	N—Cl	1.730(8)	FNCl	105(1)		
NF_2CF_3	N—F	1.371(4)	FNF	105.3(5)	GE+MW, r_{av}	[28]
	C—N	1.476(5)	CNF	104.1(7)	r	
$NF(CF_3)_2$	N—F	1.378(12)	CNC	116.6(6)	GE, r_α^0	[28]
	C—N	1.446(4)	CNF	104.8(7)		
NCl_3	N—Cl	1.754(2)	ClNCl	107.8(4)	MW, r_s	[29]
	N—Cl	1.759(2)	ClNCl	107.1(5)	GE, r_g	[30]
NCl_2CH_3	N—Cl	1.74(2)	ClNCl	108(2)	GE	[9]
	C—N	(1.47)*	CNCl	109(2)		
$NCl(CH_3)_2$	N—Cl	1.749(1)	CNCl	108.0(1)	MW, r_0	[31]
	C—N	1.476(1)	CNC	(110.7)*		
$NHClCH_3$	N—Cl	1.750(3)	ClNC	109.4(2)	MW, r_s	[32]
	C—N	1.474(5)	ClNH	102.8(2)		
NH_2Cl	N—Cl	1.748(1)	ClNH	103.7(3)	MW, r_s	[33]
	N—H	1.017(5)	HNH	107(2)		

*Accepted value.

The N–C bond lengths decrease systematically in the fluoroamine series CF_3NF_2 > $(CF_3)_2NF$ > $(CF_3)_3N$ (Tables 1 and 2).

The configuration of the bonds formed by the nitrogen atom in aromatic amines is sensitive to the influence of substituents. According to microwave data, the molecule of aniline $C_6H_5NH_2$ (A) is non-planar.[34] The angle of displacement of the N–C_{arom} bond from the plane NX_2 (Φ) is 37.5°, and the angle HNH is 113°, indicating that the configuration of the bonds formed by the nitrogen atom is pyramidal:

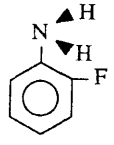


(A) (B)

For the related molecule of *p*-diaminobenzene (B),[35] the angle Φ characterising the pyramidal character of the configuration of the bonds formed by the nitrogen atom is slightly greater [43(4)°] than that in aniline (37.5°), but the conformation of the molecule (B) is similar to that of aniline. Of the other geometric parameters of these molecules, the N–C bond lengths [1.402(2) Å in (A) and 1.424(5) Å in (B)] and the $CC_{NH_2}C$ valence angles [119.4(2)° in (A) and

119.8(2)° in (B)] are noteworthy. The N–C bond length in arylamines is much shorter than that in alkylamines and halogenoalkylamines. The deformation of the valence angle in the benzene ring at the amine nitrogen atom is slight.

Microwave data have been published, characterising the configuration of the bonds formed by the amine nitrogen atom in the molecules of *o*-, *m*-, and *p*-$XC_6H_4NH_2$ (X = F,[36–38] Cl[39–41]), *p*-$FC_6H_4NHCH_3$,[42] $C_6H_5NHCH_3$,[43,44] and $C_6H_5N(CH_3)_2$‡.[45] The complete structures of these molecules have not been determined, however. Of all the fluorine-substituted anilines, *o*-$FC_6H_4NH_2$ [36] is the one for which the parameters characterising the geometry of the amino-group are closest to those for non-substituted aniline; it is followed by *m*-$FC_6H_4NH_2$,[37] and the greatest deviations are observed for *p*-$FC_6H_4NH_2$.[38] It is suggested[36] that since an intramolecular hydrogen bond H...F may be formed, the conformation of the *o*-$FC_6H_4NH_2$ molecule probably differs from that of aniline.



When one or two H atoms in the amino-group of *p*-$FC_6H_4NH_2$ are replaced by a CH_3 group, the configuration of the bonds formed by the nitrogen atom is flattened considerably.

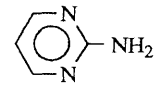
Molecule	$C_6H_5NH_2$	*m*-$FC_6H_4NH_2$	*n*-$FC_6H_4NH_2$	*n*-$FC_6H_4NHCH_3$	*n*-$FC_6H_4N(CH_3)_2$
Angle HNX, ° (X = H, CH_3)	113.1(2)	115.0	112	115.6	114
Angle of displacement of the N–C_{arom} bond $\bar{\phi}$, °	37.5(2)	36.2	46.4	18.3	27

In the series of chloro-substituted anilines, on going from *o*-$ClC_6H_4NH_2$ [39] to *p*-$ClC_6H_4NH_2$ [41] the angle Φ characterising the pyramidal nature of the configuration of the bonds formed by the nitrogen atom increases from 34.5° to 41.4°.

The structure of another two arylamines, $(C_6H_5)_3N$ [47] and $C_6H_5NCH_2CH_2$,[48] can be considered. In the triphenylamine molecule the valence angles at the nitrogen atom are 116(2)°, that is the configuration of the bonds formed by the nitrogen atom is flattened considerably, as in N-fluoromethylamines, but in the N-phenylethyleneimine molecule the nitrogen atom, firmly fixed in the ring, has a pyramidal structure, and the angle of displacement of the N–C_{arom} bond from the plane of the three-membered ring is ~55°. The conformation of the $C_6H_5NCH_2CH_2$ molecule is similar to that of aniline and dimethylaniline. The electron diffraction studies of the $(C_6H_5)_3N$ and $C_6H_5NCH_2CH_2$ molecules, however, were carried out in the sixties, with an accuracy lower than that now attainable.

‡ The $C_6H_5N(CH_3)_2$ molecule has also been studied by electron diffraction,[46] but the accuracy of the determination of the parameters is low.

2-Aminopyrimidine



is stereochemically similar to arylamines.[49] The molecule of this compound is flatter than the aniline molecule, and the angle of displacement of the N–C_{arom} bond from the plane of the NH_2 group is 27°. The N_{amine}–C bond length [1.33(1) Å] is shorter than that in $C_6H_5NH_2$.

Thus the configuration of the bonds formed by the nitrogen atom in arylamines varies from pyramidal to almost planar, depending on the substituents on the nitrogen atom and to some extent on the substituents in the benzene ring.

Comparison of aliphatic and aromatic amines shows that $r(N-C)_{aliph} > r(N-C)_{arom}$ and $\bar{\alpha}_N(aliph) < \bar{\alpha}_N(arom)$ ($\bar{\alpha}_N$ is the average value of the valence angle at the nitrogen atom).

There are almost no published data on enamines of the type $R^1R^2N-CR^3=CR^4R^5$ in the gas phase. In a microwave study of vinylamine $CH_2=CHNH_2$,[50] the complete structure could not be determined. By making a number of assumptions it was possible to obtain, with a low accuracy, only the N–C bond lengths [1.397(30) Å and the C=C–N angle [125.2(20)°], and also the angle between the N–C bond and the continuation of the bisector of the HNH angle [θ = 34(5)°].

The amides of carboxylic acids $RC(O)NH_2$ and their derivatives form a separate class of compound. The central fragment in amide molecules contains the N–C(O) bond. A knowledge of the geometry of this fragment is of considerable importance for establishing the structure of the peptide group in polypeptides.

The geometry of the molecules of the simplest amides has been studied by spectroscopic and diffraction methods and in considerable detail. The nitrogen atom in the >NC(O) group has a planar bond configuration. The N–C(O) bond is ~0.1 Å shorter than the N–CH_3 bond. The bond lengths in the molecules are different in the gas phase and in the crystal; the N–C(O) bond is 0.07 Å longer, and the C=O bond ~0.4 Å shorter, in the gas phase than in the crystal.

Detailed data on the structure of amides in the gas phase are given in a book by Naumov and Kitaeva.[51]

2. Monomeric compounds of amines with metals

Electron diffraction studies, carried out mainly abroad in the late eighties, provide material for generalising the characteristics of the geometric structure of monomeric compounds of amines with metals, chiefly compounds in which the metal has a low coordination number (CN).

A large proportion of these data relate to compounds containing two-coordinate metals of groups II (the *s*-elements Be and Mg, and the *d*-elements Zn, Cd, and Hg), VII, and VIII (the *d*-elements Mn, Fe, and Co), and also to compounds with the *p*-elements of group IV Ge, Sn, and Pb (Table 3). Data have also been published on compounds of amines with three-coordinate Sc, La, Ce, and Pr (*d*-elements of group III and lanthanides), and on tetra-amino-compounds of Ti, Zr, and V, a penta-amino-compound of Ta, and a hexa-amino-compound of W (*d*-elements of groups IV–VI, Table 4).

The two-coordinate state is not characteristic of the atoms of the lighter group II metals. Their compounds with amines tend to associate to give bridged systems, and the CN of the metal may reach four or more. In the compounds studied, the stability of the two-coordinate states of the atoms of these metals is ensured by the

large volume of the substituent $N[SiMe_3]_2$. Only the Hg atoms are distinguished by their inability to extend greatly their coordination sphere. The following mechanism has been proposed[61] to explain this difference in the coordination properties of the *d*-elements of group II. If the nitrogen atoms form σ-bonds with the sd_{z^2}-hybrid orbitals of the two-coordinate atoms of these elements, then since the 6*s*- and 5*d*-energy levels of the Hg atom are close to one another, there is more complete mixing for this atom, so that the Hg–N bonds are stronger than the Zn–N or Cd–N bonds. When adducts are formed, however, the degree of mixing of the *s*- and *d*-orbitals of the Hg atom decreases, the primary Hg–N bonds become weaker, and there is probably no energy gain as a reuslt of additional coordination to the metal atom, that is the structure of the adduct is unstable.

Table 3. Parameters (r_a) of monomeric amino-derivatives of two-coordinate metal atoms, obtained by gas-phase electron diffraction.

Molecule	Bond lengths, Å		Valence angles, °			Refs.
	E–N	N–Y	NEN	ENY	YNY	
			Group II			
$Be[N(SiMe_3)_2]_2$	1.562(24)	1.722(7)	180	115.4(4)	129.2(7)	[52]
$Mg[N(SiMe_3)_2]_2$	1.91(3)	1.703(6)	180	114.0(12)	132(2)	[53]
$Zn[N(SiMe_3)_2]_2$	1.824(14)	1.728(7)	180	114.8(10)	130.4(20)	[54]
$Cd[N(SiMe_3)_2]_2$	2.03(2)	1.727(7)	180	114.0(6)	132.0(12)	[55]
$Hg[N(SiMe_3)_2]_2$	2.01(2)	1.732(9)	180	116.0(10)	128(2)	[56]
			Groups VII and VIII			
$Mn[N(SiMe_3)_2]_2$	1.95(2)	1.718(6)	180	114.0(6)	132.1(12)	[57]
$Fe[N(SiMe_3)_2]_2$	1.84(2)	1.723(5)	180	114.4(5)	131.2(10)	[57]
$Co[N(SiMe_3)_2]_2$	1.84(2)	1.730(7)	180	114.7(7)	130.6(14)	[57]
			Group IV			
$Ge[N(SiMe_3)_2]_2$	1.89(1)	1.743(6)	101(2)	121.1(7)	117.8	[58]
$Sn[N(SiMe_3)_2]_2$	2.089(10)	1.74	96,0	117.3	125.4	[59]
$Sn(NMe_2)_2$*	1.996(4)	1.483(3)	95(1)	118.1(3)	123.8	[60]
$Pb[N(SiMe_3)_2]_2$	2.20(2)	1.75(1)	91(2)	119.6(8)	120.8	[58]

*The parameter r_g is given.

The presence of bulky substituents is apparently no less important for the stabilisation of monomeric structures with the two-coordinate *d*-atoms Mn, Fe, or Co and *p*-elements of group IV. The tendency of these compounds to associate is revealed by the formation of dimers in the crystal and in the gas phase. The gas-phase structure of one of these compounds, namely the dimer of the amino-derivative of tin(II) $\{Sn[NMe_2]_2\}_2$, will be examined in Section V.

For the atoms of group III metals (Sc, La, and the lanthanides), the usual CN are 7, 8, and 9, and with small bidentate ligands such as the nitrate group, even CN of 10 and 12 are possible. The bulky nature of the $N(SiMe_3)_2$ ligands is also of decisive importance for stabilising the fairly uncommon three-coordinate states of the atoms of these elements.

a. Amino-derivatives of *s*- and *d*-elements of group II and *d*-elements of groups VII and VIII

Important common characteristics of these compounds are the linearity of the N–E–N fragment, the planar configuration of the bonds formed by the amine nitrogen atom, and the orthogonal arrangement of the two pairs of terminal substituents $SiMe_3$ in the stable molecular form.

For the structures of the *d*-elements of group II (Zn, Cd, and Hg), the first two of these characteristics also follow from an analysis of the vibrational spectra of solutions[62] and the utlraviolet spectra of the gas phase.[63] The spectral data, however, do not make it possible to make a choice between the orthogonal (D_{2d}) and planar eclipsed (D_{2h}) conformations of the $Si_2N-E-NSi_2$ core. Electron diffraction data show that the equilibrium form has D_{2d} symmetry. At the same time there is a torsional motion of large amplitude round the linear chain N–E–N. The heights of the potential barriers (V_2) in the planar transition state D_{2h}, obtained for amino-derivatives of Mg, Zn, Cd, and Hg, are relatively small [3(1), 2.5(1.5), 1–2, and 2(1) kcal mol^{-1} respectively] and practically constant, at least for the derivatives of the *d*-elements.

The production of the barrier to rotation in this case might be due to the presence of dative π-bonds in the N–E–N fragment, van der Waals interactions between the ligands, or a combination of these factors. Force field calculations based on the vibrational spectra[62] show that in the molecules being considered the E–N bonds should be essentially single bonds. At the same time, if it is assumed that the other geometric parameters (other than the angle of rotation) remain unchanged in the process of internal rotation, then in the planar form D_{2h} the shortest of the distances between the Me groups, although shorter than those in the equilibrium form D_{2h}, are nevertheless greater than the sum of the van der Waals radii. Thus the existence of the barrier to internal rotaiton could be attributed to the effects of dative π-interaction rather than to steric factors. Although these electronic effects are very small, in this case they are apparently responsible for the stabilisation of the linear form of the N–E–N fragment.

It is possible to take as a geometric criterion of the multiplicity of the metal–nitrogen bond the difference between its length and that of the corresponding metal–chlorine bond.

	Be	Mg	Zn	Cd	Hg	Cl
r(E–Cl), Å	1.75	2.18	2.06	2.21	2.25	1.99
r(E–N), Å	1.56	1.91	1.82	2.03	2.01	1.76
Δ, Å	0.19	0.27	0.24	0.18	0.24	0.23

Since the nitrogen and chlorine atoms have equal electronegativities, the polar corrections for the corresponding bonds with a metal should also be equal. Since the accuracy of the determination of the Be–Cl, Be–N, Cd–Cl, Cd–N, and Hg–N bond lengths is low, it can be taken that the effect of replacing the chlorine atom by the nitrogen atom remains practically constant, and the actual changes Δ can be related to the difference between the covalent radii of the chlorine and nitrogen atoms. For metal chlorides, significant multiplicity of the metal–chlorine bonds is unlikely, since the chlorine atom cannot be a strong electron donor for a metal atom.

From the general principle that the atomic radius increases on going from a lighter to a heavier element in a group, the changes in the bond lengths E–N in the compounds of the group II elements show two anomalies (Table 3), on going from the *s*-atom Mg to the *d*-atom Zn and on going from the Cd atom to the Hg atom. Thus the Mg–N bond is 0.35 Å longer than the Be–N bond, and the Cd–N bond is 0.2 Å longer than the Zn–N bond. However, since

the effective charge on the nucleus of the Zn atom, which has a full *d*-level, is much larger, the Zn–N bond length is ~0.1 Å shorter than the Mg–N bond length. The Hg–N bond length in turn differs little from the Cd–N bond length, apparently due to a combination of the effects of *d*-contraction, *f*-contraction, and relativistic concentration.

The relatively short Be–N bond is possibly a consequence of a slight increase in dative π-interaction, if the small radius of the Be atom and its fairly high acceptor power are taken into account. Together with the increase in the inter-ligand interactions, this should lead to an increase in the barrier to internal rotation in the $Be[N(SiMe_3)_2]_2$ molecule compared with the amino-derivatives of the other group II metals.

In the compounds of the group VII and VIII metals of period IV, the change in the E–N bond lengths corresponds to the change in the atomic radius on going from a lighter to a heavier element. A characteristic feature is that within the large experimental errors the Mn–N bond length still approaches the Mg–N bond length, whereas the Fe–N and Co–N bond lengths are almost the same as the Zn–N bond length.

For the parameters of the ligand $N(SiMe_3)_2$, the Si–N bonds in some of the compounds examined are shorter than that in the $HN(SiMe_3)_2$ molecule [r_a = 1.738(5) Å[64]], whereas in others they are almost equal to this value. The observed decrease in the Si–N bond lengths is usually attributed to an increase in the polarity of the corresponding E–N bonds, which leads to an increase in the dative π-interaction between the N and Si atoms. The changes in the SiNSi valence angles in the amino-derivatives of the metals being considered relative to $HN(SiMe_3)_2$ [131.3(15)°] are slight. The large value of this angle, characteristic of these compounds, in this case is apparently determined chiefly by intra-ligand steric factors. Comparison of the data being considered with the dimeric structures of amino-derivatives of Mn and Co in the crystals shows that dimerisation is accompanied by a considerable increase in the length of the terminal E–N bonds and a decrease in the Si–N–Si valence angles in the terminal ligands by ~10°.

b. Structures with two-coordinate atoms of *p*-elements of group IV

It was noted above that the use of the bulky substituents $N(SiMe_3)_2$ makes it possible to obtain more stable monomeric compounds with two-coordinate Ge, Sn, or Pb atoms in the gas phase and in crystals. When $N(SiMe_3)_2$ groups in an Sn^{II} derivative are replaced by NMe_2, the concentration of the monomer in the gas phase decreases to 76 ± 1%.

Unlike the amino-derivatives of metals of groups II, VII, and VIII, the monomers of the *p*-elements of group IV contain non-linear N–E–N fragments (Table 3). At the same time, the planar configuration of the bonds formed by the amine nitrogen atom is preserved. Both NY_2 planes are practically perpendicular to the NEN plane.

The valence angles NEN do not exceed 101°. They decrease regularly with increase in the atomic number of E, as is characteristic of many other compounds of the elements of the main sub-groups. This corresponds to the familiar Bent's rule, according to which an increase in the difference between the electronegativities of the atom E and the substituent is accompanied by an increase in the *s*-character of the non-bonding orbitals of the atom E. It is also possible that a decisive role is here played by inter-ligand steric repulsions which are weaker for longer E–N bonds. Steric effects, however, probably have a greater influence on the E–N bond lengths. Thus the Sn–N bond in the $Sn(NMe_2)_2$ molecule is almost 0.1 Å shorter than that in the $Sn[N(SiMe_3)_2]_2$ molecule, whereas the NSnN valence angles are almost equal in the two molecules. The difference between the E^{II}–N and E^{IV}–N bond lengths obtained for Ge and Sn derivatives is half of this value (see Table 3 and Ref. 2). Comparison shows that the Sn–N bond in the $Sn(NMe_2)_2$ molecule is only ~0.05 Å shorter than that in the $Sn(NMe_2)_4$ molecule. Overall, the change in the E^{II}–N bond lengths in the structures being considered reflects the gradual increase in the atomic radius on going from a lighter to a heavier element.

In the crystalline phase the E–N bond lengths of the monomers are practically the same as those in the molecules in the gas phase, whereas the NEN angles are larger by 10° or more and become less sensitive to the nature of the atom E. This is probably related to a change in the orientation of the ligands in the crystal, since the form of the molecule produced in the gas phase is not favourable for effective packing. This change leads to the production of shorter intramolecular contacts, and the resulting strain is compensated by an increase in the angle NEN. The relative ease of the change in the orientation of the $N(SiMe_3)_2$ groups on going from the gas to the crystalline phase may indicate that the potential function of the internal rotation is flat.

c. Amino-derivatives of *d*-elements of group III and the lanthanides

X-Ray diffraction data show that the amino-derivatives of group III elements $E[N(SiMe_3)_2]_3$ are monomeric. All the compounds $E[N(SiMe_3)_2]_3$ can be divided into two groups differing in the configuration of the EN_3 fragments. This separation also corresponds to the characteristics of the electronic structure of the metal atom. The derivatives of the *p*-elements (Al, Ga, In, Tl) have a planar core EN_3, and D_3 symmetry for the molecule as a whole. In the derivatives of the group III *d*-elements and the lanthanides studied, the configuration of the EN_3 fragment is pyramidal, with valence angles NEN equal to 115.5 (Sc), 117.8(1) (Nd), and 116.6° (Eu).

On going to the gas phase there are appreciable changes in the configuration of the environment of the atoms of the group III *d*-elements and the lanthanides (Table 4).

Electron diffraction data show that in the Sc derivative the configuration of the ScN_3 fragment becomes almost planar, whereas in the compounds of La, Ce, and Pr (nearest neighbours of Nd in the periodic table) the EN_3 fragment is much more pyramidal than in the crystal. The measured dipole moments and the infrared spectra also indicate that the solutions contain molecules with a planar ScN_3 fragment,[72] and the vibrational spectra of the derivatives of the lanthanides Pr and Nd confirm that their structures are non-planar in the crystal, in the gas phase, and in solutions.[73] The values of the valence angles NEN found in the crystal are very close to one another, and possibly determine the molecular form most favourable for crystal packing. The relative ease with which changes take place in these angles with change in the state of the substance apparently indicates a flat form for the potential function of the inversion of the central atom E in these systems.

The pyramidal configuration of the ScN_3 fragment, produced in the solid phase by the effects of crystal packing forces, is accompanied by a change in the geometry of the ligands. The Si–N bonds become much longer [1.751(2) Å], and the angle SiNSi

Table 4. Parameters of monomeric amino-derivatives of metals with coordination numbers from three to six, obtained by gas-phase electron diffraction.

Molecule	Parameter	Bond lengths, Å		Valence angles, °			Refs.
		E–N	N–Y	NEN	ENY	YNY	
				Group III			
$Sc[N(SiMe_3)_2]_3$	r_a	2.02(3)	1.715(8)	119.5(15)	116(1)	128(2)	[65]
$La[N(SiMe_3)_2]_3$	r_a	2.36(3)	1.692(13)	110(3)		128(4)	[66]
$CeN(SiMe_3)_2]_3$	r_a	2.33(4)	1.696(15)	112(3)	108(2)*anti* 123(2)*syn*	129(4)	[67]
$Pr[N(SiMe_3)_2]_3$	r_a	2.31(4)	1.705(15)	113(3)	108(2)*anti* 123(2)*syn*	129(4)	[67]
				Group IV			
$Ti(NMe_2)_4$	r_a	1.917(3)	1.461(2)	114.2(17) 2-fold 107.2(9) 4-fold	124.3(3)	113.3	[68]
$Zr(NMe_2)_4$	r_g	2.071(11)	1.461(4)	110.5(25) 4-fold 107.4(48) 2-fold	124.3(6)	111.3(12)	[69]
				Groups V and VI			
$V(NMe_2)_4$	r_a	1.879(4)	1.457(3)	114.1(1) 4-fold 100.6(5) 2-fold	123.2(3)	113.6	[68]
$Ta(NMe_2)_5$	r_g	1.922(12)ax. 2.034(12)bas.	1.461(11)	114.1(35)ax.-bas. 75.5(2)bas.		110.7(40)	[70]
$W(NMe_2)_6$	r_g	2.035(5)	1.453(4)	180	125.6(4)	108.9(8)	[71]

Note. The prefixes anti- and *syn*- are used to characterise the relative arrangement of the $SiMe_3$ groups and the atom of the metal E relative to the N_3 plane in the triamino-derivatives of Ce and Pr; ax. and bas. denote the axial and basal Ta–N bonds in the pentakis(dimethylamino)tantalum molecule and the valence angles between them; 2-fold and 4-fold denote the two-fold and four-fold valence angles NEN in the tetra-amino-derivatives of Ti, Zr, and V (S_4 symmetry); the difference between them is that the S_4 axis lies in the planes of the two-fold angles.

becomes much smaller [121.6(4)°]. These changes are apparently due to Me...Me contact repulsion between neighbouring $N(SiMe_3)_2$ groups.

A consequence of the steric requirements of the bulky $N(SiMe_3)_2$ ligands may be their propeller-like configuration, found in the gas phase, relative to both the planar EN_3 fragment in $Sc[N(SiMe_3)_2]_2$ [angle of rotation 55(2)°] and the pyramidal EN_3 fragment in the derivatives of Ce [42(5)°] and Pr [47(5)°]. In the crystalline phase the configuration is practically unchanged, and the angle of rotation is ~50°.

d. Amino-derivatives of *d*-elements of groups IV–VI

The stability of the monomeric structures of the derivatives of the *d*-elements of groups IV–VI decreases on going from a lighter to a heavier element in a group, and this is usually related to the change in the covalent radii. Studies of benzene solutions of amino-derivatives of Ti and Zr showed, in particular, that the $Ti(NMe_2)_4$ molecules are monomeric in solution, whereas $Zr(NMe_2)_4$ gives an equilibrium monomer–dimer mixture.

Many derivatives of tantalum and tungsten in higher oxidation states also exist as binary or pseudo-binary compounds. Data on the structure of the stable monomeric amino-derivatives of these elements are therefore of considerable interest. The study of the structure of $V(NMe_2)_4$ is also important in relation to the influence of change in the configuration of the electron cloud of the central atom on the structure on going from the d^0-compounds of Ti and Zr to the d^1-compound of V.

One of the most significant characteristics of the state of amine nitrogen atoms, namely the bond configuration, is practically planar in all the structures studied (Table 4); this is apparently determined by the $p_\pi - d_\pi$-interaction of the nitrogen atom with the metal atom. At the same time, changes in the covalent radius of the metal atoms and also in their coordination numbers may have a significant influence on the form of the potential function of the wagging–inversion motion of the amino-group, which may be more or less flat, depending on steric factors.

The covalent radius of the Zr atom (1.45 Å) is much larger than those of the atoms of Ti (1.32 Å) or W (1.30 Å). The flatter potential function of the inversion of the amino-group in the $Zr(NMe_2)_4$ molecule compared with $W(NMe_2)_6$ is indicated by the much larger mean amplitude of the vibrations for the distances Zr...C [0.162(8) Å] compared with W...C [0.085(1) Å], whereas the amplitude of the vibrations for the C...C distances is almost the same in the two molecules.

The observed difference in the Zr–N and Ti–N bond lengths (0.154 Å) corresponds closely to the difference between the covalent radii given above. At the same time, for the bonds Zr–N and W–N the value of this difference obtained experimentally (0.036 Å) is much smaller than the estimated value. Thus the actual radius of the W atom in the $W(NMe_2)_6$ molecule is underestimated, and the

deviation is possibly due to inter-ligand steric interactions. The W–N bond length in the gas phase [2.035(5) Å] agrees with that found in crystalline $W(NMe_2)_6$ [2.032(25) Å[71]]. The $W(NMe_2)_6$ molecules in both phases have core symmetry T_h, with orthogonal planar $C_2N-W-NC_2$ fragments and linear N–W–N chains.

The molecular structures of the tetra-amino-derivatives of Ti, Zr, and V studied have S_4 symmetry. The configuration of the EN_4 fragment in these derivatives deviates considerably from T_d symmetry, particularly in the V compound. This is confirmed by spectral data.[74] The dihedral angles NENC characterising the rotation of the plane of the amino-group relative to the NEN plane containing the S_4 axis varies in these structures from 51(1) (Ti) to 69(9) (Zr) and 71(2)° (V).

The increase in the radius of the central metal atom on going from Ti to Zr possibly explains the slightly smaller deviation of the NZrN valence angles from the tetrahedral value (109.47°). It has been pointed out[69] that the deviation of the symmetry of the core of the $Zr(NMe_2)_4$ molecule from T_d cannot be regarded as statistically significant. Moreover, the large error in the determination of the valence angles of the ZrN_4 fragment and the fact that changes in these angles (not exceeding ±2°) have no influence on the values of the other parameters suggest that the ZrN_4 fragment is appreciably non-rigid and easily deformed.

The results of the X-ray diffraction study of the diamagnetic d^2-structure of $Mo(NMe_2)_4$ are of interest.[75] The crystal cell contains two independent molecules having symmetry close to D_{2d} (angle N–Mo–N–C ~90°). The value of the NMoN angles in these molecules, however, varies completely arbitrarily from 107.3(2)° to 112.5(2)° [average value 109.5(19)°], that is it is determined chiefly by intermolecular forces. The influence of the d^2 electron configuration of the central Mo atom on the structure of $Mo(NMe_2)_4$ is apparently less significant.

Table 5. Microwave and electron diffraction data for imino-derivatives.

Molecule	Method	Parameter	N=C, Å	X–N=C, °	Refs.
$HN=CH_2$	MW	r_s	1.273	110.4	[76]
$FN=CF_2$	MW+GE	r_α^0	1.274(6)	107.9(2)	[77]
$ClN=CCl_2$	GE	r_α^0	1.266(5)	117.1(4)	[78]
$Me_3CN=CH-CH=NCMe_3$	GE	r_a	1.283(6)	122.8(15)	[79]

In the opinion of authors cited,[68,69] the conclusion that the EN_4 core of tetra-amino-derivatives of Ti, Zr, and V undergoes deformations of large amplitude is confirmed by the appreciable values of the mean amplitudes of the vibrations obtained for the N...N distances [0.22(3), 0.14(3), and 0.19(4) Å in the derivatives of Ti, V, and Zr respectively]. However, the large experimental error most probably reflects the fact that the contribution of the N...N distances to the diffraction pattern is too small to be determined reliably against the background of the stronger or more numerous E...C, C...C, and N...C contributions.

The same feature apparently makes meaningless the discussion of the observed differences in the ratios between the values of the two-fold and four-fold valence angles NEN in the compounds studied (see Table 4), including the discussion of the possible influence of change in the configuration of the electron cloud of the central atom.

The $Ta(NMe_2)_5$ molecule has C_{2v} symmetry, and the TaN_5 fragments form a distorted square pyramid. A characteristic feature of the structure is that the axial Ta–N bond is 0.1 Å shorter than the basal bonds.

Table 6. Electron diffraction data (r_a) for carbodi-imide derivatives.

Molecule	N=C, Å	X–N=C, °	τ, °*	Refs
$H_3SiN=C=NSiH_3$	1.206(5)	150.6(12)**	—	[80]
$Me_3SiN=C=NSiMe_3$	1.216(4)	142.0(11)	44(2)	[81]
$H_3GeN=C=NGeH_3$	1.184(9)	138.0(5)	75	[82]
$Me_3GeN=C=NGeMe_3$	1.219(5)	131.4(9)	59(4)	[81]
$F_2PN=C=NPF_2$	1.240(5)	132.8(5)	55	[83]

*Dihedral angle between the planes XNC and CNX.
**The authors cited[80] assume that the equilibrium value of the Si–N=C valence angle is 180°, so that the Si–N=C=N–Si fragment is linear.

III. Imino-, carbodi-imido-, and azino-derivatives

In the imino-derivatives (Table 5) the N=C bond length changes little under the influence of substituents. The valence angle at the nitrogen atom, however, increases considerably on going from the $FN=CF_2$ molecule to $ClN=CCl_2$ and then to $Me_3CN=CH-CH=NCMe_3$, because of the appreciable steric interactions.

In the carbodi-imides (Table 6) the carbon atom forms bonds of the cumulene type, so that the N=C bonds in these compounds are shorter than those in the imines. The marked increase in the valence angle X–N=C (X = Si, Ge, P) compared with that in the imines may be due to the steric and electronic effects of the attachment of the Si, Ge, and P heteroatoms to the nitrogen atom. An interesting feature is that on going to the bulkier $SiMe_3$ and $GeMe_3$ substituents the X–N=C angle becomes much smaller than that in the SiH_3 and GeH_3 derivatives. Thus the observed increase in the valence angles Si–N=C and Ge–N=C is apparently due to the stereoelectronic effects of the Si and Ge atoms.

The cumulene bond system in allene $H_2C=C=CH_2$ has D_{2d} symmetry, with a dihedral angle H–C=C=C–H of 90°. In the carbodi-imide derivatives, however, the arrangement of the terminal groups is characterised by a much smaller dihedral angle. The investigation of this feature requires more systematic studies and quantum-chemical calculations.

Azino-derivatives (Table 7) are diene systems, that is classical conjugated double bond systems. As in derivatives of butadiene, the central N–N bond in these compounds is shorter than that in hydrazine [1.449(2) Å[88]]. The decrease in the length of the N–N bond in the molecule of the azine of formaldehyde $H_2C=N-N=CH_2$ (~0.05 Å), however, is smaller than the decrease in the length of the C–C bond in butadiene compared with ethane (0.07 Å^2). This can be attributed to the smaller coordination number of the N atom. The experimental average values of the N–N bond lengths (r_g, r_a) in halogen-substituted azines of formaldehyde (Table 7) were determined with a fairly large uncertainty, so that regularities in the changes cannot be established.

Table 7. Electron diffraction data for azino-derivatives.

Molecule	Parameter	Bond lengths, Å		Angles, °		Refs.
		N=C	N–N	N–N=C	C=N–N=C	
$H_2C=N-N=CH_2$	r_g	1.280(2)	1.402(4)	114.5(4)	180*	[84]
$F_2C=N-N=CF_2$	r_a	1.264(7)	1.421(12)	112.7(9)	153(5)**	[85]
$Cl_2C=N-N=CCl_2$	r_g	1.267(4)	1.389(9)	117.3(10)	139(7)*	[84]
$Br_2C=N-N=CBr_2$	r_g	1.274(10)	1.381(23)	117.4(27)	121(9)*	[84]
$MeH_2=N-N=CHMe$	r_a	1.277(4)	1.436(12)	110.5(7)	160—180**	[86]
$F_3C-C=N-N=C-CF_3$ $F_2C-CF_2-CF_2$	r_a	1.257(11)	1.349(19)	121.9(7)	52.4	[87]

*The value of the dihedral angle at the minimum of the potential function of the internal rotation is given (the angle 180° corresponds to the planar *anti*-form). For $H_2C=N-N=CH_2$, an MP2/6-31GF** calculation[84] gave another shallower minimum at an angle C=N–N=C of ~90° (see text).

**The effective value corresponding to averaging with respect to the twisting vibration of large amplitude relative to the N–N bond is given (see text).

Non-empirical quantum-chemical calculations in the Hartree–Fock approximation with 6-31GF** [85] and 6-31GF* [84] basis sets indicate a regular decrease in the length of this bond in the equilibrium *trans*- or close to *trans*-conformations of the azine of formaldehyde and its tetrafluoro- and tetrachloro-derivatives (from 1.40 to 1.39 and 1.37 Å respectively). According to these calculations, the change in the N–N bond length in the internal rotation is 0.04 Å. In the case of the azine of formaldehyde, the N–N bond length is shortest in the *gauche*-form (1.37 Å), and in the planar *cis*- and *trans*-forms with a predisposition towards conjugation it increases to 1.41 Å and 1.40 Å, whereas in the halogen derivatives there is a regular change from the smallest value in the *cis*-form to the largest value in the *trans*-form.

The conformation of C=N–N=C is of considerable interest. The results of experiments and calculations indicate that the potential functions of the internal rotation of the azine of formaldehyde and its halogen derivatives have a fairly flat surface in a wide region close to the *trans*-form and a high barrier in the *cis*-position. The height of the barrier is 14.6 kcal mol^{-1} for the molecule of the azine of formaldehyde (MP2/6-31GF** calculation), and 14.2 kcal mol^{-1} and 26.5 kcal mol^{-1} for the tetrafluoro- and tetrachloro-derivatives (MP2/6-31GF*//6-31GF*).[84] Calculation at the Hartree–Fock level gives a value for the barrier which is only 2 kcal mol^{-1} higher. These values are 2–3 times the values obtained by calculations at the Hartree–Fock level for the heights of the barriers in butadiene, glyoxal, and their fluoro-derivatives (see Ref. 85 and references therein). The form of the potential curve in the flat region and the position and number of the minima on it depend to a significant extent on the substituents present in the molecule. Thus for the molecule of the azine of formaldehyde, in addition to the principal minimum corresponding to the planar *trans*-form, non-empirical calculation[84] also gives a weak minimum in the region of the *gauche*-form (the dihedral angle C=N–N=C is ~90°), with an energy 0.75 kcal mol^{-1} higher. The barrier to the transformation from the *trans*- to the *gauche*-form is very low, only 0.85 kcal mol^{-1}.

In contrast to this, according to the calculations,[84] for the $F_2C=N-N=CF_2$ molecule the minimum corresponding to the *trans*-position is the only one. An electron diffraction study of the fluorinated azine of formaldehyde[85] gave for the angle C=N–N=C the effective value 153(5)°, due to averaging with respect to a twisting vibration of large amplitude. This non-planarity of the average configuration is related to the fact that the equilibrium *trans*-form has planar symmetry. In the twisting vibrations, rotation through the same angle in different directions from the plane of symmetry leads to two equivalent configurations. Thus the averaging with respect to configurations which is obtained in the analysis of the electron diffraction data without allowance for the vibration of large amplitude (using the so-called static model) leads to an effective non-planar configuration of the molecule.

The potential function of the internal rotation of the $Cl_2C=N-N=CCl_2$ molecule has a minimum in the region of the *gauche*-form. The experimental value of the dihedral angle C=N–N=C at the positon of the minimum [139(7)°], obtained by analysis with allowance for the twisting vibration of large amplitude (using the so-called dynamic model), shows good agreement with the value obtained in a quantum-chemical calculation.[84] Estimation of the height of the barrier in the transition state corresponding to the planar *trans*-form, however, gives a value not exceeding 0.1 kcal mol^{-1}.

According to electron diffraction data, the height of the barrier to rotation in the planar *trans*-form [1.4(12) kcal mol^{-1}] in the $Br_2C=N-N=CBr_2$ molecule should be much greater than that in the chlorine analogue, and the minimum of the potential function in the *gauche*-position corresponds to a greater deviation from the *trans*-form [121(9)°].

In the *trans*-conformations of the Cl- and Br-derivatives of the azine of formaldehyde there is considerable steric repulsion between the Cl or Br atoms and the lone pairs of the N atoms in the *cis*-position to them. The importance of steric factors is indicated by the appreciable increase, found by calculations,[84,85] in the N–N=C valence angles on going from the *trans*- to the *cis*-form for the azine of formaldehyde and its tetrafluoro- and tetrahcloro-derivatives (by 10, 15, and 20° respectively).

IV. Nitro-compounds

C-, N-, and O-nitrocompounds, with CNO_2, NNO_2, and ONO_2 groups, are distinguished. Structural data on nitro-compounds, obtained up to 1979, have already been reviewed.[89] The present

Table 8. Principal geometric parameters of the molecules of various nitro-compounds in the gas phase, from gas-phase electron diffraction data (r_g structure).

Compound	Bond lengths, Å				Valence angles, °			φ_{NO_2}, °	Refs.
	C⩬C	C–N	N=O	C–X*	ONO	CC_NC	CC_XC		
$C_6H_5NO_2$	1.399(3)	1.486(4)	1.223(3)	—	125.3(2)	123.4(3)	—	13(1)	[92]
o-$ClC_6H_4NO_2$	1.387(2)	1.462(12)	1.226(2)	1.721(3)	123.6(10)	121.4(12)	121.7(7)	34(3)	[93]
m-$ClC_6H_4NO_2$	1.388(3)	1.442(10)	1.243(3)	1.746(6)	122.6(10)	123.0(15)	121.5(12)	13(6)	[94]
n-$ClC_6H_4NO_2$	1.388(4)	1.469(19)	1.233(4)	1.710(7)	123.2(16)	122.6(12)	120.4(10)	19(5)	[95]
2,6-$(NO_2)_2C_6H_3Cl$	1.395(3)	1.447(4)	1.229(2)	1.712(5)	123.0(3)	121.6(4)	118.9(6)	54(1)	[96]
1,3,5-Cl_3-2,6-$(NO_2)_2C_6H$	1.400(6)	1.469(15)	1.228(7)	1.705(6)	129.2(30)	120.9(14)	119.7(5)	65(1)	[97]
sym-$C_6Cl_3(NO_2)_3$	1.399(3)	1.464(6)	1.217(2)	1.699(4)	131.4(24)	120.6(5)	119.4(15)	79(1)	[98]
o-$BrC_6H_4NO_2$	1.386(3)	1.494(14)	1.218(3)	1.894(6)	128.6(15)	120.4(24)	119.6(12)	43(3)	[99]
m-$BrC_6H_4NO_2$	1.394(3)	1.448(14)	1.238(3)	1.865(8)	121.8(14)	121.4(15)	121.4(10)	25(5)	[99]
n-$BrC_6H_4NO_2$	1.399(3)	1.455(12)	1.240(4)	1.895(7)	125.0(7)	121.6(6)	122.6(6)	19(3)	[100]
2,6-$(NO_2)_2C_6H_3Br$	1.393(3)	1.468(9)	1.229(3)	1.899(9)	125.6(9)	122.7(9)	117.1(12)	58(3)	[99]
sym-$C_6Br_3(NO_2)_3$	1.402(7)	1.455(16)	1.242(5)	1.886(6)	133.8(20)	121.6(11)	118.4(11)	77(1)	[101]
o-$IC_6H_4HO_2$	1.398(3)	1.472(22)	1.238(4)	2.096(10)	122.4(9)	122.3(14)	118.6(11)	60(4)	[102]
m-$IC_6H_4NO_2$	1.392(2)	1.490(17)	1.227(3)	2.100(9)	124.0(5)	124.0(10)	121.9(7)	14(5)	[102]
n-$IC_6H_4NO_2$	1.397(2)	1.459(14)	1.229(2)	2.103(8)	122.4(6)	122.2(6)	122.2(4)	16(1)	[103]
sym-$C_6(CH_3)_3(NO_2)_3$	1.397(2)	1.487(8)	1.221(2)	1.482(11)	126.8(6)	123.5(8)	116.5(8)	72(1)	[104]
sym-$C_6(OH)_3(NO_2)_3$	(1.393)	1.491(7)	1.231(3)	1.371(7)	124.9(8)	120.0(11)	118.4(6)	12(7)	[105]
o-$NO_2C_6H_4SeBr$	1.396(6)	1.466(24)	1.229(8)	1.917(11)	124.8(6)	123.7(6)	—	0	[106]
o-$NO_2C_6H_4SCl$	1.397(3)	1.459(9)	1.229(3)	1.776(5)	125.1(40)	123.0(3)	—	0	[107]

*X is the substituent in addition to the NO_2 group (X = Cl, Br, I, CH_3, OH, SeBr, SCl).

review gives the results of the study of the structure of molecules of nitro-compounds of all three types, published in recent years. Among the C-nitro-compounds, most attention has been paid to aromatic halogeno- and polynitrobenzenes, and also nitrobiphenyls.

1. Aromatic C-nitro-compounds

The principal geometric parameters of a number of nitrobenzene derivatives in the gas phase are given in Table 8.

As noted earlier,[4,5,90] the geometry of aromatic nitro-compounds is determined by the mutual influences in the nitro-group–benzene ring–substituent system. Subsequent studies have confirmed this conclusion.

All compounds of this type show deformation of the benzene ring under the influence of the nitro-groups and other substituents (Cl, Br, I, CH_3). The addition of electron-acceptor groups to the benzene ring leads to an increase in the valence angle of the *ipso*-carbon atom.[90,91] This is shown most clearly in *para*- and *meta*-substituted nitrobenzenes. In the molecules of 1-chloro- and 1-bromo-2,6-dinitrobenzenes, the nitro-groups are responsible for the deformation of the benzene ring, and the influence of the chlorine and bromine atoms is slight. The competing influence of the nitro-groups and the chlorine (bromine) atoms is shown most clearly in the *sym*-trihalogenonitrobenzenes. Unfortunately, the experimental errors do not make possible a more detailed discussion of this question.

The greatest deformation of the benzene ring is observed in the *sym*-$C_6(CH_3)_3(NO_2)_3$ molecule, where the electron-acceptor NO_2 groups and the electron-donor CH_3 groups supplement one another. This can be seen by comparing the data in Table 9.

Table 9. Valence angles CC_XC (°) in the molecules of $C_6X_3(NO_2)_3$ and $C_6H_3X_3$.

X	$C_6X_3(NO_2)_3$		Refs.	$C_6H_3X_3$	Refs
Cl	119.4(5)	[120.6(5)]*	[98]	122.0(2)	[108]
Br	118.4(11)	[121.6(11)]	[101]	120.4(8)	[109]
CH_3	116.5(8)	[123.5(8)]	[104]	118.2(2)	[110]
NO_2	—	—	—	123.0(9)	[111]

*The values of the angles $CC_{NO_2}C$ are given in square brackets.

In the series of aromatic nitro-compounds given in Table 8, the C⩬C bond lengths in the benzene ring are shorter than in non-substituted benzene. This applies to *o*-chloro and *o*-bromonitrobenzenes (this feature was previously noted for *sym*-trinitro- and *p*-dinitrobenzenes[111]). In *sym*-$C_6Cl_3(NO_2)_3$, however, where the accuracy of the determination is fairly high, there is no decrease in the C⩬C bond length (in non-symmetrical nitro-derivatives, some non-equivalence of the C⩬C bonds may be assumed, but it is impossible to detect it experimentally by gas-phase electron diffraction). The average C⩬C bond length in nitrobenzenes is independent of the number of NO_2 groups.

Analysis of the parameters of the nitro-group shows that the scatter in the N=O bond lengths (average value 1.228 Å) does not exceed 0.015 Å. The average value of the angle ONO is 125°, but the values of this angle in nitrobenzene derivatives differ considerably.

The $C-NO_2$ bond lengths have been determined with fairly large errors. The average value of $r(C-NO_2)$ is 1.47 Å. Because of the relatively large errors in the determintion of $r(C-NO_2)$ and the small changes in this quantity, it is difficult to establish the influence of substituents on the length of this bond or the dependence of $r(C-NO_2)$ on the angle of rotation of the nitro-group. The changes in $r(C-N)$ and the angle φ_{NO_2} for halogenonitrobenzenes (Table 8) show no definite relationship between them.

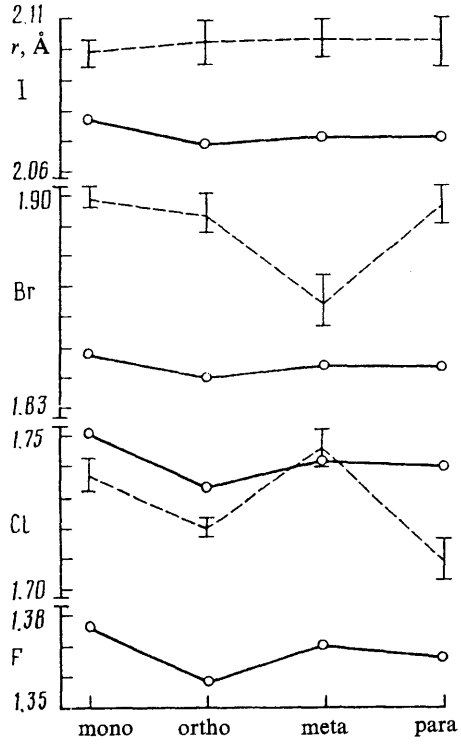


Figure 1. Dependence of the experimentally determined bond length $r_g(C-X)$ (broken line) and the corresponding bond length $r_e(C-X)$ (continuous line) obtained from non-empirical calculations on the position of X in halogenonitrobenzenes; the calculations were carried out using the basis sets 6-31GF for X = F, 3-21GF* for X = Cl, and STO-3GF* for X = Br and I respectively; the notation "mono" refers to the halogenobenzene, and "ortho", "meta", and "para" to the positions of the substituents X = F, Cl, Br, and I in the halogenonitrobenzenes.

Figure 1 gives the dependence of the C–X bond lengths (X = F, Cl, Br, I) on the positions of the substituents X in halogenonitrobenzenes.

Under the influence of the nitro-group in the molecules of chloronitrobenzenes there is a slight decrease in the length of the C–Cl bond in the *ortho*- and *para*-substituted nitro-derivatives compared with chlorobenzene [1.737(6) Å [112]]. This decrease in the C–Cl bond length is not observed in *m*-chloronitrobenzene.

The decrease in the C–Cl bond length in the *o*-chloronitro-derivatives is confirmed by the data for 1-chloro-2,6-dinitrobenzene, *sym*-trichloronitrobenzene, and 1,3,5-trichloro-2,6-dinitrobenzene.

The C–Br bond lengths in *o*- and *p*-bromonitrobenzenes are practically the same as that in bromobenzene [1.899(3) Å].[113] This is confirmed by the data for 1-bromo-2,6-dinitrobenzene. The shortest C–Br bond length was found experimentally in *m*-$BrC_6H_4NO_2$; this does not correspond to the trend detected for other molecules and by *ab initio* calculations.[102]

For iodonitrobenzenes, the changes in the C–I bond lengths are very small. As in the case of the C–Br bond, nitro-groups in the *ortho*- or *para*-positions have no influence on the C–I bond length.

Figure 1 also gives the results of *ab initio* calculations for the molecules of fluoro-, chloro-, bromo-, and iodonitrobenzenes. The largest changes in the C–X bond lengths were obtained for fluoronitrobenzenes, and the smallest for iodonitrobenzenes.

It is of interest to follow the influence of nitro-groups on the C–Cl, C–Br, and $C-CH_3$ bond lengths (in Å) by comparing the data obtained for the symmetrical 1,3,5-derivatives:

	C–Cl	C–Br	$C-CH_3$
1.3.5-$C_6H_3X_3$	1.734(2)	1.877(4)	1.509(2)
1.3.5-$C_6(NO_2)_3X_3$	1.699(4)	1.886(6)	1.482(11)

The C–Cl and $C-CH_3$ bond lengths decrease on going to the nitro-derivatives. Because of the relatively large experimental errors, the difference for the C–Br bond is statistically insignificant.

According to microwave data,[114] the potential of the internal rotation of the NO_2 group in the nitrobenzene molecule has a minimum at $\varphi_{NO_2} = 0°$, that is for the planar configuration of the molecule. The barrier to the rotation is 2.9 kcal mol^{-1}. Electron diffraction study makes it possible to determine the average value of the dihedral angle between the planes of the benzene ring and the nitro-group; for $C_6H_5NO_2$ the value does not coincide with the equilibrium value, and is equal to 13°.[92] The same situation apparently arises for the *meta*- and *para*-derivatives of nitrobenzene, where the minimum of the potential of the internal rotation of the NO_2 group corresponds to 0°, and the non-planar conformations, detected by electron diffraction, are related to the twisting vibrations of the nitro-groups. Allowance for these vibrations leads to planar equilibrium models with a barrier to rotation $V_2 \simeq 4-5$ kcal mol^{-1}.[115]

In the molecules of the *ortho*-derivatives of nitrobenzene there is considerable steric hindrance, and the equilibrium configurations are appreciably non-planar. Thus in the *ortho*-dinitro-derivatives and 1-halogeno-2,6-dinitro-derivatives the experimentally determined conformations are close to the equilibrium ones.

In the *sym*-trinitro-substituted benzenes $C_6(NO_2)_3X_3$ (C = Cl, Br, CH_3) the average dihedral angles are ~80°. If the equilibrium configuration corresponds to an angle $\varphi_{NO_2} = 90°$, it may be expected that vibrational effects will destroy the high symmetry of the equilibrium configuration, leading to a decrease in the dihedral angle φ_{NO_2}. Thus *ortho*-substituted nitrobenzenes are sterically "crowded" molecules, and the greatest steric strain is produced in the *sym*-tribsubstituted nitrobenzenes.

The decisive factor lowering the steric strain is the rotation of the nitro-group through the angle φ. Comparison of the shortest distances Cl...O, Br....O, CH_3...O and correspondingly Cl...N, Br...N, CH_3...N with the sums of the van der Waals radii for *sym*-hexasubstituted nitrobenzenes shows that the distances between the

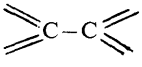
non-bonded atoms X...O are close to the sums of the van der Waals radii, whereas the X...N distances are much smaller than the corresponding sums.

The molecules of *o*-$(NO_2)C_6H_4SCl$ and *o*-$(NO_2)C_6H_4SeBr$ are planar, with internuclear distances O...S (2.36 Å) and O...Se (2.39 Å) shorter than the sums of the van der Waals radii [3.13 Å (O...S) and 3.30 (O...Se)]. The planar conformations of these molecules, in which the S and Se atoms approach the NO_2 group, may be the result of conjugation of the lone pairs of S and Se with the electronic system of the nitro-group (donor–benzene ring–acceptor system), and also of intramolecular coordination of the oxygen of the nitro-group to these atoms.

The planar conformation has also been established for the $C_6(OH)_3(NO_2)_3$ molecule. This result is consistent with earlier data obtained for the molecules of *o*-nitrophenols in the crystalline phase, in which an intramolecular hydrogen bond is assumed. By analogy, the existence of a bond of this type may be expected for the molecules in the gas phase. The distance $r(O_{NO_2}...H_{OH})$ [1.55(5) Å] between neighbouring NO_2 and OH groups is much shorter than the sum of the van der Waals radii of the H and O atoms (2.45 Å), and the angle O–H...O is 116°.

The very few structural data for nitro-derivatives of biphenyl relate mainly to the crystals. Until recently only one compound, 6,6′-dinitrobiphenyl-2,2′-dicarboxylic acid, had been studied in the gas phase.[116]

As in the case of non-substituted biphenyl,[117] a characteristic feature of the molecules of nitro-derivatives of biphenyl is the rotation of one benzene ring relative to the other round the central



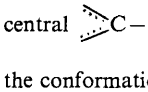
bond. Thus in the "free" molecule of 6,6′-dinitro-biphenyl-2,2′-dicarboxylic acid the angle of rotation of the rings φ_{C-C} is 71°, and the angle of rotation of the nitro-group φ_{NO_2} is 30°.

Among the nitro-derivatives of biphenyl studied in the crystalline state, 2-nitrononafluorobiphenyl[118] shows the largest angle of rotation of the rings (86°). In this compound there is also appreciable rotation of the nitro-group (56°). Compounds with nitro-groups in the *para*-positions (4-nitrobiphenyl[119] and 4,4′-dinitrobiphenyl[120]) show an almost coplanar arrangement of these groups and the benzene ring, that is their conformation is analogous to that of *para*-derivatives of benzene. Within the experimental error, the length of the central C–C bond in the nitro-derivatives of biphenyl is close to that in non-substituted biphenyl (1.49 Å).

A series of electron diffraction studies of the biphenyl derivatives 4,4′-dinitrobiphenyl, 2-nitrobiphenyl, and 2,2′-dinitro-4,4′-dichloro-biphenyl has now been carried out.[121–123]

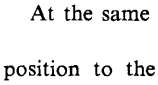
The results are compared with data for biphenyl and nitrobenzene in Table 10. For 4,4′-dinitrobiphenyl, the electron diffraction data are also compared with X-ray diffraction data.

The results supplement and confirm the previously noted geometric characteristics of the structure of nitrobiphenyls. In particular, comparison of the angles of rotation φ_{C-C} indicates that the introduction of nitro-substituents in the *para*-position to the central



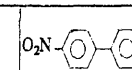
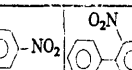
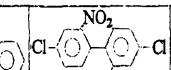
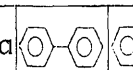
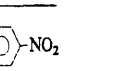
bond has no statistically significant influence on the conformation of the biphenyl fragment.

At the same time the introduction of an NO_2 group in the *ortho*-position to the



bond increases by 20° the angle of rotation of the benzene rings relative to one another (~65°), compared with non-substituted biphenyl. The highest value of the angle φ_{C-C} is observed in 2,2′-dinitro-4,4′-dichlorobiphenyl (87°), that is in the molecule with the greatest steric strain.

Table 10. Geometric parameters of the molecules of biphenyl, nitrobenzene, and nitro-derivatives of biphenyl.

Parameters						
	GE (Ref.122)	XRD (Ref.120)	GE (Ref.121)	GE (Ref.123)	GE (Ref.117)	GE (Ref.92)
Bond lengths, Å						
⟩C–C⟨	1.499(27)	1.499(16)	1.481(36)	1.507(39)	1.509(4)	—
C⋯C	1.402(2)	1.393(20)	1.395(3)	1.394(2)	1.400(5)	1.399(2)
C–N	1.479(8)	1.532(22)	1.466*	1.482(17)	—	1.486(2)
N=O	1.223(6)	1.201(18)	1.207(13)	1.220(5)	—	1.223(2)
Angles, °						
ONO	125.4(6)	128.6(24)	123.8(15)	127.8(9)	—	125.4(2)
CCNC	123.6(15)	126.9(16)	123.8*	124.8(6)	—	123.4(2)
φ_{C-C}	50.3(51)	32.7	64.8(51)	87.2(83)	44.4(12)	—
φ_{NO_2}	-25.0(48)	10.0(13)	-64.1(70)	-24.8(75)	—	13.3(10)

*Determined in agreement with experiment.

The principal difference between the structural parameters of 4,4′-$NO_2C_6H_4C_6H_4NO_2$ in the free molecule and in the crystal is observed for the central torsional angle φ_{C-C}. The other structural parameters are comparable, within the experimental error. The same conclusion was previously reached by comparing the geometries of non-substituted biphenyl in the gas phase and in the crystal.

As in the case of mono-substituted benzene derivatives, the addition of a nitro-group to the biphenyl ring leads to an increase in the endocyclic angle at the carbon atom joined to the nitro-group, compared with the trigonal value.

2. N-Nitramines (N-nitro-compounds)

In N-nitramines there is a direct interaction between the electron-donor amino-group and the electron-acceptor nitro-group. The geometry of the molecules of these compounds depends significantly on the substituents on the amine nitrogen atom.[89] We are speaking primarily of the changes in the N–N bond lengths and the pyramidal nature of the amine nitrogen atom.

Despite the fairly large number of published experimental studies of N-nitramines,[89] however, there is still no clear picture of the regularities in their structures and the energy parameters of the intramolecular motions involving inversion of the amine nitrogen atom and internal rotation about the N–N bond. The answers to many problems are not obtained by structural methods, and the unambiguous interpretation of the results is often difficult.

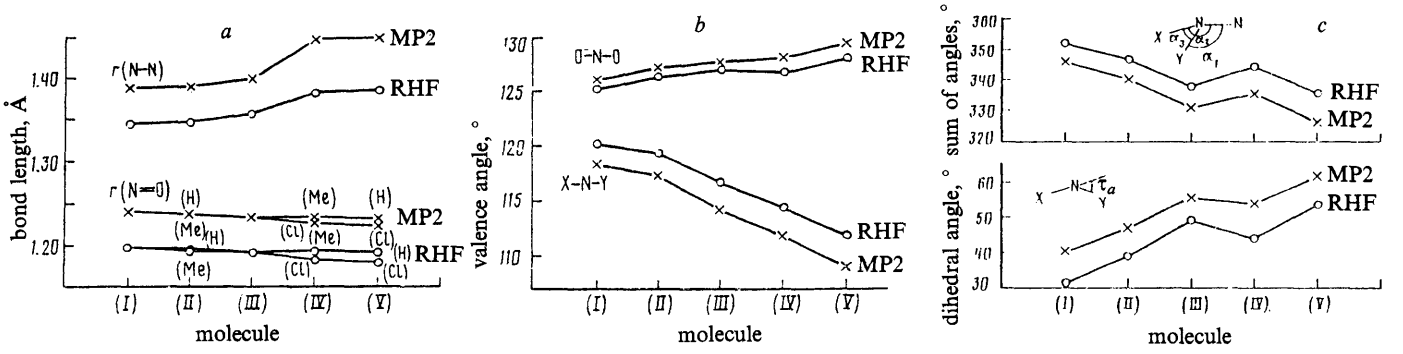


Figure 2. Influence of change in the electronegativity of the substituents on the amine nitrogen atom on the N—N and N=O bond lengths (*a*), the valence angles ONO and XNY (*b*), and the pyramidal character of the configuration of the amine nitrogen atom [the change in the dihedral angle between the NNX and NNY planes (τ_a) and the sum of the valence angles at the nitrogen atom ($\Sigma\alpha_N$)] (*c*) in the N-nitramines (I)—(V), from the results of RHF/6-31GF* and MP2/6-31GF* calculations.

a. Non-empirical quantum-chemical calculations for N-nitramines

These compounds, which are important for theoretical and practical chemistry, can now be studied systematically using another powerful instrument, namely quantum-chemical calculations. The results of calculations for five N-nitramines, H_2NNO_2, $MeNHNO_2$, $ClNHNO_2$, $MeNClNO_2$, and Me_2NNO_2,[124,125] carried out by the restricted Hartree—Fock (RHF) method with allowance for electron correlation using second-order Möller—Plesset theory (MP2), are of interest. The standard basis set 6-31GF*, which has proved effective in similar studies,[8,126—128] was used.

Many structural parameters of amino-derivatives, including the valence angles at the nitrogen atom, are reproduced with this basis set within the experimental error of their determination, even at the RHF level. Allowance for electron correlation in the MP2 approximation largely removes the discrepancies between the calculated and experimental lengths of multiple bonds and neighbouring bonds. Simultaneously, however, the pyramidal nature of the amine nitrogen atom is overestimated slightly.

Analysis of the results reveals a trend towards a coordinated change in the geometric parameters with change in the effective electronegativity of the substituents on the amine nitrogen atom. With increase in the electronegativity of the substituents, that is with decrease in the electron-donor properties of the substituted amino-group, there is an increase in the N—N bond length, a decrease in the N=O bond length, an increase in the pyramidal character of the bond configuration of the amine nitrogen atom, and an increase in the non-planarity of the nitro-group. All this can be regarded as a consequence of a decrease in the $p-\pi$ conjugation between the lone pair of electrons of the amine N atom and the π-system of the NO_2 group.

This is clearly demonstrated by the graphs in Fig. 2 giving the changes in the geometric parameters, where the discrete points on the abscissa correspond to the positions of the compounds in order of increasing electronegativity of the substituents: Me_2NNO_2 (I), $MeNHNO_2$ (II), H_2NNO_2 (III), $MeNClNO_2$ (IV), and $ClNHNO_2$ (V). The greatest difference in the N—N bond lengths (up to 0.06 Å) is observed on going from molecule (I) to (V) (Table 11).

An interesting feature is that with increase in the electronegativity of the substituents X and Y on the amine nitrogen atom the valence angles ONO and XNY change synchronously, but in opposite directions away from the value 120°; the angle ONO increases with increase in the electronegativity of the substituents X and Y (this can be related to the change in the electron density distribution with decrease in the N=O bond length), whereas the angle XNY decreases.

Table 11. N—N bond lengths in N-nitramines, from experimental data and the results of non-empirical quantum-chemical calculations for the equilibrium structures (ES) and the transition states of the inversion (TS_{inv}) of the amino-group and internal rotation (TS_r) (in Å).

Molecule	Experiment				RHF/6-31GF* calculation (Refs. 124, 125)			MP2/6-31GF* calculation (Refs. 124, 125)		
	method	parameter	r(N—N)	Refs	ES	TS_{inv}	TS_r	ES	TS_{inv}	TS_r
Me_2NNO_2	GE	r_a	1.382(3)	[129]	1.344	1.326	1.424	1.387	1.359	1.463
$MeNHNO_2$	GE	r_a	1.381(6)	[130]	1.346	1.325	1.422	1.389	1.358	1.463
H_2NNO_2	MW	r_0	1.427(2)	[131]	1.356	1.327	1.421	1.399	1.361	1.462
	MW	r_0	1.381	[130]						
$MeNClNO_2$	GE	r_a	1.469(5)	[130]	1.381	1.343	1.442	1.447	1.379	1.506
$ClNHNO_2$	–	—	—	—	1.384	1.341	1.440	1.449	1.380	1.511
$MeN(NO_2)_2$	GE	r_a	1.480(5)	[132]						

The systematic increase in the dihedral angle τ_a between the planes NNX and NNY and the simultaneous decrease in the sum of the valence angles at the amine N atom, together with the changes in the angle XNY, indicate that the pyramidal nature of the amine nitrogen atom increases with increase in the electronegativity of the substituents.

Unlike the experimental data (Table 12), the results of the calculation give a pyramidal bond configuration for the amine nitrogen atom for all the molecules studied. Thus the interaction of

the amine nitrogen atom with the nitro-group, unlike that for other functional groups (the acyl group and the nitrosyl group[126–128]), does not lead to a planar bond configuration for the amine nitrogen atom in the equilibrium state of the molecule.

Table 12. Dihedral angle NNX/NNY in N-nitramines (τ_a, °), from experimental data and the results of non-empirical quantum-chemical calculations of the equilibrium structures (ES) and the transition states of internal rotation (TS_r).

Molecule	Experiment			RHF/6-31GF* calculation (Refs. 124, 125)		MP2/6-31GF* calculation (Refs 124, 125)	
	method	τ_a	Refs.	ES	TS_r	ES	TS_r
Me_2NNO_2	GE	0	[129]	31.2	56.1	40.4	60.7
$MeNHNO_2$	GE	not determined	[130]	39.1	62.5	47.0	66.0
H_2NNO_2	MW	53.0	[131]	49.1	67.2	55.5	71.9
	MW	45.0	[130]				
$MeNClNO_2$	GE	51.4	[130]	44.1	59.2	53.8	64.4
$ClNHNO_2$	–	—	—	53.6	67.2	61.7	72.3

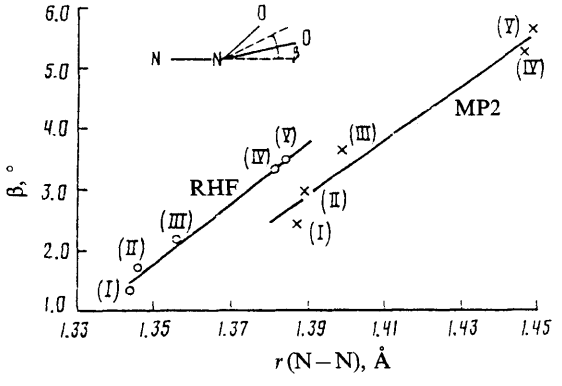


Figure 3. Relationship between the N–N bond length and the angle of displacement of the N–N bond from the ONO plane (β) in the N-nitramines (I)–(V), from the results of RHF/6-31GF* and MP2/6-31GF* calculations.

The deviation from the planar configuration of the nitrogen atom of the nitro-group is defined by the angle of displacement of the N–N bond from the ONO plane (β), the change in which is practically proportional to the change in the N–N bond length. Figure 3 give the dependence of the angle β on r(N–N) for the N-nitramines studied. It is consistent with the concept of $p-\pi$-conjugation: the greater the conjugation and the shorter the N–N bond becomes, the greater the flattening of the bond configuration of the nitrogen atom of the nitro-group. An equally simple relationship is not obtained for the angle of displacement of the N–N bond from the plane of the amine nitrogen atom XNY. This may indicate that change in the steric factors has a significant influence on the configuration of the amine group.

To characterise the potential function of the displacement of the N–N bond from the plane of the nitro-group, the geometry of the molecules Me_2NNO_2, $MeNHNO_2$, and $ClNHNO_2$ was optimised for a fixed planar configuration of the NNO_2 fragment. The total energies of the optimised models were greater than that of the equilibrium form. It is significant that in all cases there were no imaginary normal-vibration frequencies. This indicates that the planar form of the nitro-group in the N-nitramines studied does not correspond to transition states. Cordell[133] obtained for the Me_2NNO_2 molecule the potential curve for the displacement of the N–N bond from the ONO plane, which has a single minimum at an angle of displacement of the N–N bond from the plane of the nitro-group equal to 1.2°, and which can be approximated by a function close to harmonic. Thus the motion being considered is the wagging vibration.

Analysis of the results of the calculation of the transition states for the inversion of the amino-group (TS_{inv}) and internal rotation about the N–N bond (TS_r) leads to the following important conclusion. The flattening of the bond configuration of the amine nitrogen atom during inversion, and the deviation of the structure of the molecule from the equilibrium form during internal rotation, are accompanied by a significant change in the other geometric parameters. Particularly marked changes are undergone by the N–N bond lengths, which are 0.06–0.08 Å longer in TS_r than in the equilibrium forms (see Table 11).

In addition, the transition state of the inversion shows a decrease in the N–N bond length, an increase in the valence angle XNY, and a slight increase in the N–O bond lengths, and the transition state of the internal rotation shows a significant increase in the pyramidal nature of the configuration of the amine nitrogen atom (see Table 12) and a decrease in the N–O bond lengths.

Roughly speaking, the planar transition state of the inversion of the amino-group should promote an increase in $p-\pi$-conjugation, whereas the perpendicular form of the transition state of the internal rotation is unfavourable for this interaction. In this connection it is of interest that the observed relaxational changes in the N–N bond lengths and other parameters during inversion or internal rotation take place in coordinated fashion and in accordance with the concept of $p-\pi$-conjugation. Moreover, the coordinated nature of the changes in the parameters in the intra-molecular motions observed in this case apparently has the same basis as the changes examined above in the parameters of the same structures as a result of the influence of the electronegativity of the substituents on the electron density distribution.

In contrast to the equilibrium forms of molecules (I)–(V), where the N–N bond lengths change regularly with change in the extent of the conugation, in TS_{inv} and TS_r the lengths of these bonds are determined almost entirely by the presence or absence of the Cl-substituent.

The graphs in Fig. 4 give the dependence of the heights of the barriers to inversion (V_i) and rotation (V_r) in the N-nitramines (I)–(V) on the electronegativity of the substituents on the amine nitrogen atom. Both methods of calculation (RHF and MP2) reveal the same trend in the changes in V_i and in V_r; the RHF calculation gives higher values than MP2 for V_r, and lower values for V_i. The height of the barrier to inversion in the H_2NNO_2 molecule, obtained by the MP2 calculation (3.1 kcal mol^{-1}), effectively reproduces the

experimental value of 2.7 kcal mol^{-1}.[135] The last value is at present the only experimentally determined energy characteristic of intramolecular motion in N-nitramine molecules.

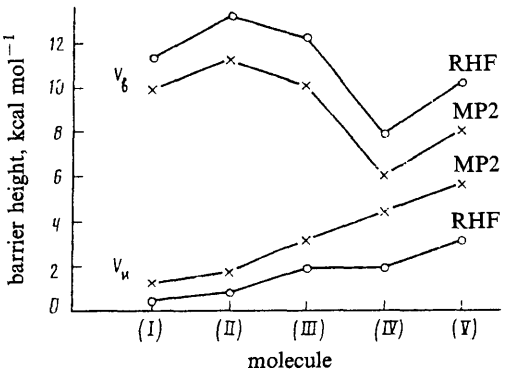


Figure 4. Changes in the heights of the barriers to inversion of the amine nitrogen atom (V_i) and internal rotation about the N–N bond (V_r) in the nitramines (I)–(V), from the results of RHF/6-31GF* and MP2/6-31GF* calculations.

The results show that the greater the pyramidal nature of the amino-group in the equilibrium state of the molecule, the higher the barrier to pyramidal inversion and in general the lower the barrier to internal rotation about the N–N bond.[8] The relationship is more complex for the barrier to rotation, however. This may reflect changes in the contributions of steric factors to the rotation potential. All estimates of the barriers to inversion of the amine nitrogen atom lie in the range 0.4–6.0 kcal mol^{-1} (for comparison, the barrier to inversion has the values 5.8 for ammonia, 2.0 for cyanamide, and 10.3 kcal mol^{-1} for diethylochloroamine[134–136]). The barriers to internal rotation in N-nitramines are 6–13 kcal mol^{-1}, that is they are 1.5–2 times lower than those for amides and N-nitrosamines.[127,128,137–140]

The existence of conjugation in the equilibrium forms of nitramines, as in other amino-derivatives with unsaturated substituents, may be indicated by the flattening of the pyramid of the bonds of the amino-group and the decrease in the N–N bond length. This is accompanied by a lowering of the barrier to inversion of the amine nitrogen atom and a raising of the barrier to internal rotation about the N–N bond. The effect of conjugation in nitramines, however, is less marked than that in amides and nitrosamines.[8] The appreciable change in the geometric parameters in the transition states compared with the equilibrium state may indicate an increase in conjugation during inversion, and breakdown of the $p-\pi$-conjugation on rotation about the N–N bond.

Finally, another interesting result of the calculation may be noted. The inversion of the amine nitrogen atom is coordinated with the flattening of the nitro-group. For a fixed planar configuration of the amino-group, optimisation of the other geometric parameters invariably leads to a planar configuration of the bonds formed by the nitrogen atom in the nitro-group. In the equilibrium states, however, as already noted, the configuration of the bonds formed by the nitrogen atom of the nitro-group is slightly pyramidal, and the degree of pyramidal character correlates well with the change in the N–N bond length.

Table 13. Structural parameters of some of the simplest N-nitramines.

Parameter	$CH_3(CH_2=CH)NNO_2$ (Ref.141)	$(CH_2Cl)_2NNO_2$ (Ref.142)	$(CH_2Cl)CH_3NNO_2$ (Ref.143)	$(CH_3)_2NNO_2$ (Ref.129)
Bond lengths, Å				
N=O	1.213(3)	1.216(3)	1.212(2)	1.223(2)
N–N	1.385(8)	1.422(5)	1.424(5)	1.382(3)
C–N	1.432(15) (vinyl) 1.459(15) (methyl)	1.443(4)	1.476(9)	1.460(3)
C–Cl	—	1.803(4)	1.809(4)	—
Angles, °				
ONO	128.0(21)	128.0(14)	127.5(10)	130.4(13)
NNC_{CH_3}	113.5(12)	116.3(4)	116.6(6)	116.2(3)
CNC	124.1(10)	124.8(9)	127.0(9)	127.6(6)
NCCl	—	111.6(5)	107.7(9)	—
φ_{NO_2}	2(18)	2.6(15)	32.9(29)	0
φ_{CH_2}	—	10.8(17)	–4.3(18)	—

b. Electron diffraction data

Work on the determination of the structure of the simplest N-nitramines in the gas phase includes gas-phase electron diffraction studies of the molecules of $(CH_2Cl)_2NNO_2$ and $CH_3(CH_2=CH)$. $.NNO_2$ (Table 13). For comparison, Table 13 also gives the parameters of the $(CH_3)_2NNO_2$ and $(CH_2Cl)CH_3NNO_2$ molecules.

In all these molecules the effective configuration of the amine nitrogen atom is planar. The CNC angle in these molecules is much larger than that in alkylamines. The influence of the Cl atom of the chloromethyl groups in $(CH_2Cl)_2NNO_2$ and $(CH_2Cl)CH_3NNO_2$ on the nitroamine fragment is slight.

In the examination of the conformation of these molecules, the following should be noted. In the $(CH_2Cl)CH_3NNO_2$ molecule, the chloromethyl group is oriented in such a way that the ClCN plane is approximately perpendicular to the CNC plane. The same orientation of the CH_2Cl group is observed in the $(CH_2Cl)_2NNO_2$ molecule, and the C–Cl bonds are on different sides of the C_2NNO_2 plane. For the $CH_3(CH_2=CH)NNO_2$ molecule, the most probable conformation is that with the *trans*-arrangement of the NO_2 and $CH=CH_2$ groups. In this molecule, conjugation between the vinyl and nitroamine fragments apparently does not influence the geometric parameters.

Until recently there were no published data on the structure of cyclic nitramines in the gas phase. Electron diffraction data have now been obtained on the structure of 1,3,5-trinitro-1,3,5-triazacyclohexane [$(CH_2NNO_2)_3$, RDX], 1,3-dinitro-1,3-diazacyclopentane [$CH_2(CH_2NNO_2)_2$, DDCP], and N-nitropyrrolidine [$(CH_2)_4NNO_2$, NP].[144] These molecules are of interest since in their five- and six-membered rings the possibilities for change in the endocyclic angles are limited, and this may lead to appreciable deviation from the planar bond configuration of the amine nitrogen atom. The actual conformation of the rings is also of interest.

The results (Table 14) show that the six-membered ring in the RDX molecule has the "chair" conformation with the nitro-groups in the axial position. The assumed C_3 symmetry is consistent with the experimental data.



Table 14. Structural parameters of cyclic N-nitramines.[144]

Parameters	RDX	DDCP	NP
Bond lengths, r_g, Å			
C–N	1.464(6)	1.483(8)	1.477(8)
N–N	1.413(5)	1.393(8)	1.363(4)
N=O	1.213(2)	1.226(2)	1.225(2)
Angles, °			
CNC	123.7(6)	109.7(17)	110.3(14)
NNC	116.3(5)	114.8(8)	116.0(11)
Σ_N^*	356(3)	339.3	342.3
NCN	109.4(6)	109.7(17)	—
NCC	—	100.2(24)	99.6(4)
ONO	125.5(10)	128.2(18)	126.3(19)

*Sum of the valence angles at the nitrogen atom.

The five-membered ring in DDCP has the "half-chair" conformation (assuming C_2 symmetry for the molecule), and that in NP has the "envelope" conformation. In both molecules (DDCP and NP) the nitro-groups are in the equatorial positions. The angles of displacement of the N–N bond from the CNC plane vary from ~20° in RDX to ~40° in DDCP and NP.

Comparison of the principal geometric parameters of the cyclic nitramines studied and of dimethylnitramine shows that the CNN angles in all four molecules are the same within the experimental error. At the same time the CNC angle in RDX is slightly smaller than the corresponding angle in $(CH_3)_2NNO_2$, and those in DDCP and NP show an even sharper decrease. This leads to a change in the bond configuration of the amine nitrogen atom from almost planar in dimethylnitramine to pyramidal in the five-membered cyclic molecules of DDCP and NP. The RDX molecule occupies an intermediate position in this series.

In the cyclic nitramines studied, no increase in the N–N bond length with increase in the pyramidal nature of the bond configuration of the nitrogen atom is observed.

3. O-Nitrates (O-nitro-compounds)

The molecular structures of O-nitro-compounds in the gas phase have been less extensively studied than those of C- and N-nitro-compounds. The geometric parameters of the $HONO_2$, O_2NONO_2, CH_3ONO_2, and $C_2H_5ONO_2$ molecules are given in Table 15.

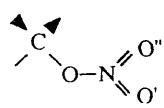
A difference in the parameters is observed only for the N_2O_5 molecule. In this molecule, the two NO_2 groups joined through the central oxygen atom undergo twisting vibrations of large amplitude. The potential energy minimum corresponds to equal torsional angles $\tau_1 = \tau_2 = 30°$ (measured from the planar conformation). The torsional movements are correlated so that an increase in one of the angles τ is accompanied by a decrease in the other.

Table 15. Geometric parameters of the O-nitro-compounds $XONO_2$ (X = H, NO_2, CH_3, C_2H_5).

Parameter	$HONO_2$	O_2NONO_2	CH_3ONO_2	$CH_3CH_2ONO_2$		
	MW, r_0 (Ref.145)	GE, r_α (Ref.146)	MW, r_s (Ref.147)	GE, r_g (Ref.148)	NC (Ref.148)*	MB (Ref.149)**
Bond lengths,						
C–O	–	–	1.437(5)	1.444(4)	1.447	1.430
N–C	–	–	–	1.520(4)	1.512	1.528
N–O	1.406(3)	1.492(4)***	1.402(1)	1.406(4)	1.412	1.407
N=O′	1.203(3)	1.183(2)***	1.208(5)	1.208(3)***	1.219	
N=O″	1.210(3)		1.205(5)		1.224	1.215
Valence angles, °						
XON (X=H, N, C)	101.9(10)	111.8(6)	112.7(3)	113.0(6)	113.2	111.0
O=N=O	130.0	133.3(6)***	129.5(5)	129.6(17)	129.9	131.0
O–N=O′	113.9(3)	113.4(4)***	112.4(3)	112.2(10)	112.6	111.0
O–N=O″	116.1(3)		118.1(3)	118.2(7)	117.5	118.0
CCO	–	–	–	106.0(10)	104.7	109.5

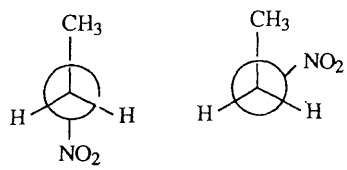
**Ab initio* calculation, MP2/6-31GF*.
**Assumed structure.
***The average value is given.

The nitric acid molecule is planar. In methyl and ethyl nitrates, the core also has a planar structure:



In $HONO_2$, CH_3,ONO_2, and $C_2H_5ONO_2$ the valence angles O–N=O are different; the angle O–N=O″ is larger than the angle O–N=O′. In methyl and ethyl nitrates the difference between these angles is 6°.

The structure of ethyl nitrate in the gas phase has been studied by gas-phase electron diffraction and microwave, infrared, and Raman spectroscopy. The data obtained by all these methods show that ethyl nitrate is a mixture of two rotational forms (*trans* and *gauche*), if rotation about the C–O bond is considered; the *trans*-form is more stable, by ~0.6 kcal mol^{-1}.



According to GE data, the concentration of the *gauche*-form is about 20%. The angle of rotation about the C–O bond in this form is about 100° (if the angle of rotation for the *trans*-form is taken as 0°).[148]

A separate group of O-nitro-compounds is formed by the metal nitrates. The monovalent metal nitrates MNO_3 (M = Cs, Rb, Tl) (Table 16) in the gas phase contain a planar bidentate NO_3 group, and the metal atom lies on the bisector of the angle O(1)NO(1′):

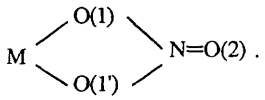


Table 16. Geometric parameters of metal nitrates.

Compound	N–O(1), Å	N=O(2), Å	O(1)NO(1′), °	Refs.
$RbNO_3$		1.252(3)*	115(6)	[150a]
$CsNO_3$		1.252(5)*	117(5)	[150b]
$TlNO_3$		1.254(8)*	114.(5)	[150c]
$Cu(NO_3)_2$	1.298(3)	1.205(5)	113.5(6)	[151]
$Zr(NO_3)_4$	1.284(7)	1.184(10)	—	[152]
$Sn(NO_3)_4$	1.281(5)	1.179(8)	—	[152]
$CrO_2(NO_3)_2$	1.254(4)	1.193(4)	112.2(4)	[153]
$Be_4O(NO_3)_6$	1.298(4)	1.185(5)	117.0(9)	[154]

*The average of the N–O(1) and N=O(2) bond lengths is given.

The $MONO_2$ fragment is also planar in the nitrates of copper $Cu(NO_3)_2$, zirconium $Zr(NO_3)_4$, and tin $Sn(NO_3)_4$. In $Cu(NO_3)_2$ the copper atom lies in the plane of the square formed by the oxygen atoms of two bidentate NO_3 groups. The ligand atoms round the central atom in Zr and Sn tetranitrates give a distorted tetrahedral configuration.

In the $CrO_2(NO_3)_2$ molecule (C_2 symmetry) the coordination of the Cr atom is best described as a distorted octahedron, since the bidentate nitrate groups are joined asymmetrically to the Cr atom. The Cr–O–NO_2 group is slightly non-planar, with a dihedral angle between the CrON and NO_2 planes of ~16(3)°. There is apparently weak torsional motion round any of the single bonds in the –O–NO_2 groups.

The structure of $Be_4O(NO_3)_6$ deviates slightly from T_d symmetry, probably as a result of a complex intramolecular motion.

In the molecules of $Cu(NO_3)_2$, $Zr(NO_3)_4$, $Sn(NO_3)_4$, $CrO_2(NO_3)_2$, and $Be_4O(NO_3)_6$, the N–O bonds are non-equivalent; the N=O(2) bond is ~0.1 Å shorter than N–O(1). For the monovalent metal nitrates, only the average N–O bond length has been obtained. The O(1)NO(1′) valence angles in the ring are smaller than 120°.

V. Complex compounds of nitrogen

A large amount of interesting material has now been accumulated on the structure of donor–acceptor compounds of nitrogen in the gas phase. A large proportion of the structural data relates to adducts of the type $Y_3E{\leftarrow}NX_3$, where E is a group III element (B, Al, Ga). The experimental data for pyridine-containing complexes in the gas phase are fundamentally new, particularly in view of their low stability. Dimeric and trimeric amino-compounds of group III elements, lithium, and tin(II), and various derivatives of the anthrane type with an intramolecular donor–acceptor bond, have also been examined.

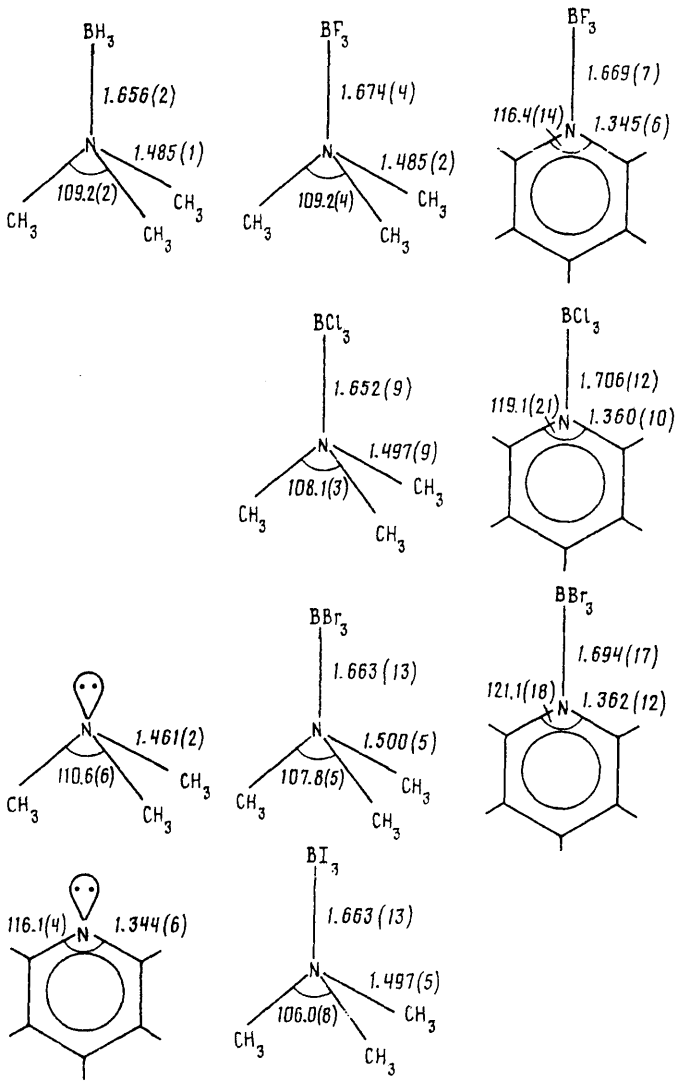


Figure 5. Comparison of the parameters of the r_g-structure of the free molecules of trimethylamine[13] and pyridine[169] and their boron adducts (see Table 17).

A new approach to the classification of the donor–acceptor bond as a unique type of bond has been proposed by Haaland,[7] who showed from an analysis of various physicochemical properties (including the geometric structure) that the donor–acceptor bond differs from a simple covalent bond.

Table 17. Adducts containing a nitrogen–boron bond.

Molecule	Parameters	Bond lengths, Å		Valence angles, °				Method	Refs.
		B–N	N–X	BNX	XNX	NBY	YBY		
$H_3B{\cdot}NH_3$	r_s	1.6576(16)	1.014(2)	110.28(14)	108.65(14)	104.69(11)	113.80(11)	MW	[155]
	r_0	1.6722(5)	1.0136(36)	109.85(23)	109.09(23)	104.53(15)	113.93(15)	MW	[155]
$H_3B{\cdot}NMe_3$	r_s	1.638(10)	1.483(10)	107.9(10)		105.32(16)		MW	[156, 157]
	r_α^0	1.651(2)	1.482(1)		109.4(2)		113.4(4)		
	r_g	1.656(2)	1.485(1)		109.2(2)		112.8(4)	GE+MW	[158]
$Me_3B{\cdot}NMe_3$	r_0	1.698*	1.470(1)	111.6(5)		108.0(15)		MW	[159]
$FH_2B{\cdot}NMe_3$	r_0	1.633(6)	1.492(9)	109.5(10)		105.3(5)		MW	[160]
			1.494(16)	(for CH_3 in the NBF plane)					
				110.1(5)		104.7(7)			
$F_3B{\cdot}NMe_3$	r_0	1.636(4)	1.476(5)	110.4(3)	108.6(2)	106.3(2)	112.4(2)	MW	[161]
	r_α^0	1.669(4)	1.481(2)		109.4(4)		113.1(3)	GE+MW	[162]
	r_g	1.674(4)	1.485(2)		109.2(4)		112.6(3)	GE+MW	[162]
	r_a	1.664(11)	1.468(10)		108.5(7)		113.1(9)	GE	[163,164]
$Cl_3B{\cdot}NMe_3$	r_α	1.650(9)	1.491(3)		108.3(3)		111.1(2)	GE	[165]
	r_g	1.652(9)	1.497(3)		108.1(3)		110.9(2)	GE	[165]
	r_a	1.659(6)	1.495(4)		108.7(5)		110.8(3)	GE	[163, 164]
$Br_3B{\cdot}NMe_3$	r_α	1.656(13)	1.483(5)		107.9(5)		110.4(3)	GE	[165]
	r_g	1.663(13)	1.500(5)		107.8(5)		110.3(3)	GE	[165]
$I_3B{\cdot}NMe_3$	r_α	1.658(13)	1.488(5)		106.2(8)		108.9(4)	GE	[166]
	r_g	1.663(13)	1.497(5)		106.0(8)		108.6(4)	GE	[166]
$F_3B{\cdot}$ 	r_g	1.669(7)	1.345(6)	r_a 116.4(14)			113.3(4)	GE	[167,168]
$Cl_3B{\cdot}$ 	r_g	1.706(12)	1.360(10)	r_a 119.1(21)			112.5(3)	GE	[168]
$Br_3B{\cdot}$ 	r_g	1.694(17)	1.362(12)	r_a 121.1(18)			111.9(3)	GE	[168]

1. Adducts containing a nitrogen–boron bond

Table 17 gives the parameters of complexes $Y_3B.NX_3$ studied in the gas phase by microwave spectroscopy (r_s, r_0) and electron diffraction (r_α^0, r_α, r_g, r_a) and by both methods. The differences between the data obtained by these two methods may be extremely large, because of the difference in the physical significance of the parameters obtained. Thus for one of the most interesting parameters, namely the NB bond length, the differences reach 0.03 Å, corresponding to the level of structural effects. In the subsequent analysis, therefore, we shall try to use comparable quantities.

When an adduct is formed, the lone pair of electrons of the nitrogen atom is partly transferred to the unoccupied orbital of the boron atom. This is accompanied by changes in the geometry of the original monomers, and the changes in the molecular parameters of the acceptor BY_3 are much greater than those for the donor NX_3.[6] We are interested primarily in the structural characteristics of the NX_3 fragment. The comparison in Fig. 5 shows that the participation of the trimethylamine molecule in complex formation as a donor leads to a significant increase in the length of the N–C bonds and a decrease in the CNC valence angles. In the adducts with boron trihalides these changes increase in the order

$$F_3B \cdot NMe_3 < Cl_3B \cdot NMe_3 < Br_3B \cdot NMe_3 < I_3B \cdot NMe_3.$$

A similar trend is observed in the change in the parameters of the nitrogen fragment of the pyridine ring on complex formation, the only but extremely significant difference being that the intra-cyclic CNC valence angle does not decrease, but increases.

The replacement of some substituents on the boron atom by others, however, does not have such a clear and systematic influence on the N–B bond length (Figs. 5 and 6). The N–B bond in the adduct $F_3B.NMe_3$ is slightly longer, whereas that in the corresponding adduct with pyridine is shorter, than those in the other members of the corresponding series of derivatives.

Although microwave studies have not given an accurate value for the N–B bond length in the adduct $Me_3B.NMe_3$ (indirect estimates give the value 1.70–1.80 Å [6]), the available data suggest that the methyl substituents in the amino-group lead to a decrease in the N–B bond length, whereas the same substituents in the acceptor fragment lead to an increase (Table 17).

The geometric parameters of adducts of the type $Y_3B.NMe_3$ in the crystalline phase differ considerably from those in the gas phase. The B–Y and N–C bond lengths become larger, and the YBY angles and, which is most important, the N–B bond lengths are smaller than those in the gas phase. For the N–B bond the difference reaches 0.05–0.10 Å.[6] This shows that in the crystal the degree of charge transfer increases considerably, and the N–B donor–acceptor bond becomes stronger. The molecules of the adducts $Y_3B.NX_3$ have the staggered conformation (C_{3v} symmetry) in both phases.

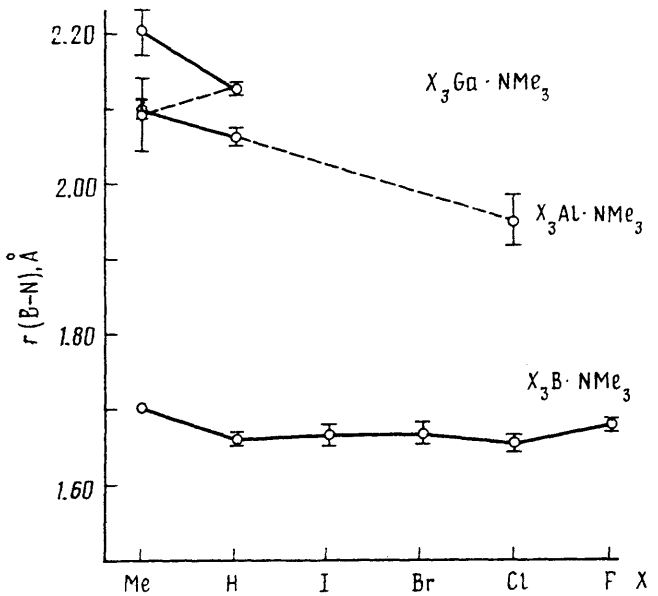


Figure 6. Influence of substitution in the acceptor group of the adducts $X_3E.NMe_3$ on the E–N bond lengths (E = B, Al, Ga; X = Me, H, I, Br, Cl, F).

The determination of the heights of the potential barriers is of considerable interest in relation to possible internal rotation about the N–B bond. Apart from anything else, these parameters are important for characterising the strength of the dative bond. The heights of the potential barriers in $Y_3B.NX_3$ cannot be estimated from the infrared and Raman spectra, however, since the twisting vibrations are not active in these spectra. The possibility of obtaining the heights of the potential barriers from an analysis of electron diffraction data using available spectral information is therefore of interest. The results of this analysis, and some microwave data, are given in Table 18.

Table 18 shows that the barriers to rotation are apparently higher in the $Cl_3B.NMe_3$ and $Br_3B.NMe_3$ molecules than in the other molecules, although the accuracy of the determination is low. The change in the height of the barriers, and also the change in the N–B bond length, most probably depend not only on the electronegativity of the substituents but also on steric factors.

2. Adducts containing nitrogen–aluminium, nitrogen–gallium, and nitrogen–halogen bonds

The structural parameters of donor–acceptor complexes containing N–Al and N–Ga bonds (mainly from electron diffraction data) are given in Table 19. They reflect more clearly the regularities established above from the analysis of the parameters of their boron analogues.

Table 18. Barriers to rotation about the dative bond N→B in the adducts $Y_3B.NX_3$.

Molecule	Height of the barrier to rotation, kcal mol^{-1}	Method	Refs.
$H_3B.NH_3$	2.03	MW	[155]
$H_3B.NMe_3$	3.4	MW	[157]
	>5	GE	[158]
$F_3B.NMe_3$	4.3(3)	GE	[162]
	6.2	GE	[164]
$Cl_3B.NMe_3$	18	GE	[165]
	13.7	GE	[164]
$Br_3B.NMe_3$	12	GE	[165]
$I_3B.NMe_3$	3.5	GE	[166]

Table 19 clearly shows the tendency for the N–Al bond length to decrease with increase in the electronegativity of the ligands on the Al atom in the order Me < H < Cl (see Fig. 6). Increase in the acceptor power of the aluminium fragment also leads to an increase in the N–C bond lengths in the donor fragment NMe_3. In turn, increase in the electronegativity of the substituent on the N atom (Me < H) is accompanied by an increase in the N–Al bond length, that is by a decrease in its strength as a result of the decrease in the donor power of the nitrogen fragment.

A characteristic feature of adducts containing N–Al and N–Ga bonds, distinguishing them from the corresponding adducts containing an N–B bond, is that complex formation leads to an increase in the CNC valence angles of the donor fragment NMe_3 (see Fig. 5). The reason apparently is that the overall increase in the N–Al and N–Ga bond lengths compared with the N–B bond lengths (by ~0.3–0.5 Å) leads firstly to a decrease in the strength of the repulsion between the bonding electron pairs of the donor and the electrons involved in the formation of the coordinate bond, and secondly to a decrease in the steric interactions between the ligands of the donor and the acceptor. In the boron complexes these factors have a more significant influence not only on the N–B bond lengths and the CNC valence angles but also on the parameters of the potential functions of the internal rotation. These interactions may determine the differences in the structural regularities examined above for the boron–nitrogen adducts with trimethylamine and pyridine (see Fig. 5).

The only results not agreeing with the other data examined in this section are those obtained in the study of the $Me_3Ga.NMe_3$ molecule.[180,181] In this compound the two key parameters characterising the structure of the adduct {the N–Ga bond length

Table 19. Adducts containing nitrogen–aluminium, nitrogen–gallium, and nitrogen–halogen bonds.

Molecule	Parameter	Bond lengths, Å		Valence angles, °				Method	Refs.
		E–N	N–X	ENX	XNX	NEY	YEY		
$Cl_3Al{\cdot}NH_3$	r_a	1.996(19)				101.2	116.35(40)	GE	[170, 171]
$Br_3Al{\cdot}NH_3$	r_a	1.997(19)	1.057(33)		114.5(40)	101.5	115.7(3)	GE	[171, 172]
$H_3Al{\cdot}NMe_3$	r_a	2.063(8)	1.476(3)	109.0(3)		104.3(11)	114.1	GE	[173]
$Me_3Al{\cdot}NMe_3$	r_a	2.099(10)	1.474(3)	109.3(4)		102.3(3)	115.6	GE	[174]
$Cl_3Al{\cdot}NMe_3$	r_a	1.945(35)	1.516(12)	112.6(15)		104.9(7)	113.6	GE	[175]
$H_3Al{\cdot}2NMe_3$	r_a	2.19(2)	1.483(5)	106.5(8)	112.6(8)			GE	[176]
$Cl_3Ga{\cdot}NH_3$	r_a	2.057(11)	1.024(12)		114.3(12)	101.1	116.4(3)	GE	[171, 177]
$Br_3Ga{\cdot}NH_3$	r_a	2.081(23)	1.061(33)		115.6(41)	100.8	116.1(3)	GE	[171, 172]
$H_3Ga{\cdot}NMe_3$	r_0	2.111(2)	1.476(20)	110(1)		102*		MW	[178]
	r_a	2.124(7)	1.482(5)	109.9(5)		102*		GE	[179]
$Me_3Ga{\cdot}NMe_3$	r_a	2.09(5)	1.484(8)	114.5(31)	104.0	99.3(22)	117.4	GE	[180]
	r_a	2.20(3)	1.485(4)		109.6	101	116.7	GE	[181]
$Br_2{\cdot}NMe_3$	r_a	1.98(3)	1.67(2)		104(2)	112(3)	—	GE	[182]
$CF_3I{\cdot}NMe_3$	r_0	2.93(2)						MW	[183]

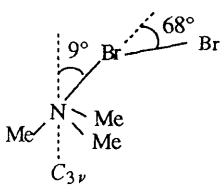
*Accepted value.

[2.09(5) Å] and the CNC valence angle (104.0°)} clearly do not correspond to the regularities examined above. Without going into details of the electron diffraction analysis, we may note that the deviation in this case is due to the unreliability of the determinaiton of the N–Ga bond length. The complexities of its determination were related to two factors: 1, the large amplitude of the vibrations for this distance, characteristic of a donor–acceptor bond, and 2, the possible decomposition of the substance on heating during the electron diffraction experiment, since dative bonds become weaker on going to the elements of the lower part of group III.[6]

An interesting feature is that the summary of the preliminary results of the structural analysis[181] gave what are apparently better justified values of these parameters, namely r(N–Ga) = 2.20(3) Å and angle CNC = 109.6°. In the crysalaline Al and Ga adducts, the molecular core also has C_{3v} symmetry, and the N–Al and N–Ga bonds, like the N–B bonds, are ~0.1 Å shorter than those in the molecules in the gas phase,[6] corresponding to an increase in the extent of charge transfer.

In the study of the structure of the double adduct $H_3Al.2NMe_3$ in the gas phase it was not possible to obtain information on the form of the molecule, apparently because of its partial dissociation. The value found for the N–Al bond length is more than 0.1 Å greater than that for the 1 : 1 adduct.

There are as yet only isolated data on adducts of trimethylamine containing a halogen atom as acceptor. The conformation of the Br_2NMe_3 molecule in the gas phase differs considerably from that found in the crystal for I_2NMe_3 (C_{3v} symmetry). The Br atom closest to the nitrogen atom deviates by 9(2)° from the three-fold axis of the NMe_3 fragment. The second Br atom deviates from the N–Br bond by a further 68(3)°.



3. Dimers and trimers of amino-compounds of various non-transition elements.

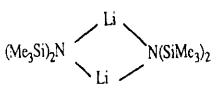
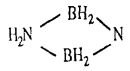
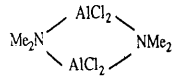
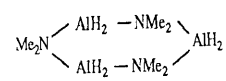
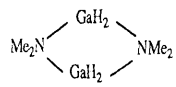
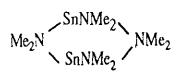
Anthrane compounds

Dative bonds involving the nitrogen atom as donor stabilise the molecular structure of the derivatives of various non-transition elements.

These structures include *n*-meric amine systems. The structures of some of the compounds have been studied in the gas phase (Table 20).

Monomeric lithium amines $LiNR_2$ with a three-coordinate nitrogen atom are extremely rare. Most lithium amines form *n*-meric cyclic systems in which the nearest lithium atoms are joined by amide bridges with four-coordinate nitrogen. Crystallographic data indicate that the $(LiN)_2$, $(LiN)_3$, and $(LiN)_4$ rings are invariably planar.[184,185]

Table 20. Dimers and trimers of the amino-derivatives of various non-transition elements.

Molecule	Conformation of the ring	Parameter	Bond lengths, Å		Valence angles, °			Method	Refs.
			E–N	N–X	ENE	NEN	XNX		
	planar	r_a	1.99(3)	1.712(7)	80(3)	100(3)	129.8(17)	GE	[184,185]
	ditto	r_s	1.558(1)	1.005(6) (r_0)	75.9(1)	97.1(6)	111.0(12) (r_0)	MW	[186]
	" "	r_a	1.961(6)	1.479(4)	92.5(4)	87.5(4)	101.3(18)	GE	[187]
	"chair"	r_a	1.970(6)	1.486(9)	113.5(27)	95(2)	112.0(21)	GE	[188]
	planar	r_a	2.027(4)	1.463(13)	90.6(8)	89.4(8)	109.6(16)	GE	[189]
	»	r_g	2.293(5)	1.483(3)	96.1(5)	83.9		GE	[60]

The only electron diffraction data for dimeric $[LiN(SiMe_3)_2]_2$ in the gas phase also indicate a planar cyclic system. The molecule as a whole has D_2 symmetry. The cores of the bridging ligands $N(SiMe_3)_2$ lie in a plane perpendicular to the plane of the ring, and the $SiMe_3$ groups of each of the ligands are arranged in a staggered conformation relative to one another. An interesting feature is that the Li–N bond length found in this case is indistinguishable from the corresponding distances in the crystalline trimeric and tetrameric lithium amines (1.97–2.00 Å [184,185]), whereas the Li–N bonds in the crystalline dimers studied show a tendency to increase, apparently as a result of the presence of the additional ligands on the Li atom.

Comparison of the electron diffraction data with the X-ray diffraction also shows that the intra-ring valence angles at the Li atom are influenced more strongly than the angles at the N atom by the dimensions of the ring. Thus the LiNLi angles change from 80° to 100° on going from the dimers to the trimers, whereas the NLiN angles change from 100° to ~170°.[184,185]

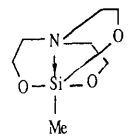
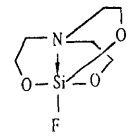
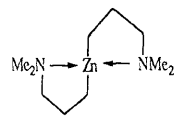
A consequence of the tetrahedral coordination of the N atom in the dimer $[LiN(SiMe_3)_2]_2$ is the slight decrease in the N–Si bond length compared with that in the $HN(SiMe_3)_2$ molecule [r_a 1.738(5) Å [64]]. The SiNSi angle in the dimeric Li amine is practically the same as the corresponding valence angle in $HN(SiMe_3)_2$ [131.3(15)° [64]].

For all the elments of the boron sub-group, the cyclic dimers $(Me_2NEH_2)_2$ are more characteristic than the monomeric structures $Me_2N{=}EH_2$ containing a multiple bond. This is due to the greater stability of the dimeric form. Experimental data obtained by various methods show that structures in which the NMe_2 groups form bridges producing a four-membered N_2E_2 ring exist in the gas phase, in solution, and in the crystalline phase.

The electron diffraction data for the Al and Ga derivatives (Table 20) are consistent with a molecular model having a planar ring and effective D_{2h} symmetry of the core $(C_2NEH_2)_2$. Since the nitrogen atoms in these compounds become four-coordinate by using their lone pair of electrons for bond formation, it is of interest to compare the E–N bond lengths in the four-membered rings and in the adducts $Y_3E.NX_3$ (see above). The comparison shows that the change to the cyclic system and the changes in the coordination spheres of the atoms lead to an appreciable decrease in the E–N bond lengths. Thus the B–N bond in aminodiborane $H_2N{\rightarrow}BH_2{-}H{\ldots}BH_2$ is ~0.1 Å shorter than in any of the adducts $Y_3B.NX_3$ studied. The Ga–N bond in the dimer $(Me_2NGaH_2)_2$ is ~0.1 Å shorter than that in the $H_3Ga.NMe_3$ molecule. The Al–N bond length in the four-membered ring of $(Me_2NAlCl_2)_2$ coincides (within the large error of the determination) with that found in the $Cl_3Al.NMe_3$ molecule, but is shorter than the dative bonds in other acyclic aminoalanes. The available X-ray diffraction data also indicate a decrease in the E–N bond lengths in the rings on going from the gas to the crystalline phase.[187,189]

The intra-ring valence angles at the Al and Ga atoms in the dimers $(Me_2NAlCl_2)_2$ and $(Me_2NGaH_2)_2$ being considered are only slightly smaller than the angles at the N atoms, so that the four-membered rings are practically square. In the six-membered ring of the aminoalane $(Me_2NAlH_2)_3$ the valence angles at the N atoms are

Table 21. Electron diffraction data for compounds of the anthrane type.

Molecule	Parameter	Bond lengths, Å			Valence angles, °		Refs.
		E–N	E–R	N–C	ENC	NSiO NZnC	
	r_g	2.453(17)	1.853(15)	1.458(6)	103.4(16)	79.0(15)	[190]
	r_g	2.324(14)	1.568(6)	1.481(8)	103.2(4)	81.3(3)	[191]
	r_a	2.392(15)	1.991(6)	1.467(3)	101(2)	82(2)	[192]

increased to a much greater extent than the angles at the Al atoms. In these rings the steric repulsion between the Al or Ga atoms is apparently greater than the interaction between the N atoms. The valence angles at the latter are greater than those found in the dimeric Li amine or aminodiborane.

Studies of trimeric aminoalanes in the gas phase (Table 19) and in the crystals[188] indicate that the valence angles at the nitrogen atoms are more easily altered parameters of the ring than the angles at the Al atom. Electron diffraction data for the $(Me_2NAlH_2)_3$ molecule show that the six-membered $(AlN)_3$ ring in it is non-planar and has the "chair" conformation (C_{3v} symmetry). Although the Al–N bond lengths found are only slightly longer than those in the chloro-substituted dimer $(Me_2NAlCl_2)_2$, the direction of the change corresponds to the influence of substituents on the E–N bond lengths observed for adducts of the type $Y_3E.NX_3$. As in the case of the dimers examined above, the Al–N bond in $(Me_2NAlH_2)_3$ is ~0.1 Å shorter than that in the adduct $H_3Al.NMe_3$. Moreover, the value obtained is 0.03–0.05 Å larger than that in various crystalline trimeric aminoalanes.[188]

The bis(dimethylamino)tin(II) dimer is less stable than the corresponding monomer (see section II). A study of this compound in the gas phase showed that its concentration in the mixture is 24 ± 1%. The Sn–N bond length in the cyclic dimer is 0.3 Å larger than that in the monomer. The four-membered $(Sn-N)_2$ ring is planar, and, as in the case of the dimeric amines of the boron sub-group, the intra-ring valence angles at the nitrogen atom are slightly greater than the angles at the tin atoms. An X-ray diffraction study, carried out in parallel with the electron diffraction study, showed that the structures of the dimer in the gas phase and in the crystal differ considerably.

The study of the structure of compounds of the anthrane type in the gas phase is also of considerable interest. At the present time, data of this kind are available for Me- and F-substituted silatranes and a chelate spiro-structure with two dative N→Zn bonds (Table 21).

Silatranes are biologically active molecules in which the properties of the substituent on the Si atom have a marked influence on the strength of the dative bond. This is confirmed by electron diffraction data. Thus electronegative substituents (for example the F atom) lead to a decrease in the N→Si bond length of more than 0.1 Å, compared with the Me-derivative. The N–C bonds in the ring systems of the F-silatrane become longer by more than 0.02 Å, as in the adducts $Y_3E.NMe_3$. The identical donor–acceptor nature of the interaction of the nitrogen atom in the silatranes and in the other classes of compound examined in this section is also revealed by the decrease in the N→Si bond length on going from the gas to the crystalline phase,[193] which is more clearly defined in the silatranes (~0.3 Å). Simultaneously, the length of the bond formed by the Si atom with the ring substituent increases by 0.02–0.05 Å.

The donor–acceptor interaction of the Zn atom with the amine nitrogen atom in its diorgano-derivatives is much weaker than that in the adducts of boron, aluminium, or gallium. Thus according to electron diffraction data, the monoligand complex $Me_2Zn.NMe_3$, which exists in the liquid phase, is completely dissociated in the gas phase even at 30 °C to $ZnMe_2$ and NMe_3,[192] and the diligand complex $Me_2Zn(NMe_3)_2$ is not known.

Nevertheless, N→Zn dative bonds are fairly stable in diorgano-derivatives of Zn with N donor atoms in the δ- or ε-positions of the substituent chain, in particular in the $Zn[(CH_2)_3NMe_2]_2$ molecule. The $(CH_2)_3NMe_2$ substituents bend to form rings, bringing the N atoms closer to the Zn atom, to give additional intramolecular coordination of the N atoms to the Zn atom with the production of a chelate structure.

A possible explanation for the instablity of the simplest adducts of Zn examined above may be that the increase in entropy associated with their dissociation plays a more significant role than the energy effect of complex formation. In contrast to this, on intramolecular coordination the entropy changes are minimal, and even a relatively low energy of complex formation is sufficient to stabilise the donor–acceptor bonds.

The weakness of the dative interaction of the N and Zn atoms is revealed by the increase in the N→Zn bond length by 0.6 Å compared with the length of the Zn—N covalent bond in the monomeric amine $Zn[N(SiMe_3)_2]_2$ (see Table 3). This is also indicated by the high value of the mean amplitude of the vibrations of the N→Zn bond [0.17(3) Å]; the amplitude of the vibrations of the Zn—C bond in the chelate ring system is only 0.073(6) Å. The transfer of the Zn-derivative from the gas to the crystalline phase is accompanied by a decrease in the N→Zn bond length (by 0.085 Å)[192] which although not so great as that in silatranes is nevertheless considerable. The bond lengths and valence angles in the five-membered rings of the chelate system of $Zn[(CH_2)_3NMe_2]_2$ are very close to those found in silatranes (Table 21).

VI. Summary

Systematic experimental studies of series of compounds are required to determine the relationships between the geometry of molecules and their chemical properties. Unfortunately, complete systems of data often are not available. This is due both to problems of synthesis and to the limited possibilities provided by the methods of studying structure. In these cases the use of non-empirical quantum-chemical calculations at a high level becomes extremely effective.

The structural data given and the regularities found reveal the important role of steric repulsion in compounds with bulky substituents. This conclusion is naturally very simple. In some cases, however, it is difficult to distinguish an interaction having a decisive influence on the configuration of a molecule. Thus the CNC valence angle at the amine nitrogen atom in methyl- and chloro-substituted N-nitramines is appreciably greater (by ~15°) than that in $(CH_3)_3N$ (~110°). At the same time, in metal amines this angle is not increased (~111°), although the configuration of the bonds formed by the nitrogen atom in these compounds, as in the Me-derivatives of N-nitramine, is planar or close to planar.

In di-imides with the cumulene bond system $\diagdown N=C=N\diagup$ the expected orthogonal configuration of the bonds formed by the nitrogen atom with substituents is not observed. This emphasises the important role of the interaction of non-bonded atoms (even at appreciable distances).

Data on nitro-aromatic derivatives and N-nitramines indicate that conjugation has an extremely limited influence on the configuration of the molecule, since the $C-NO_2$ bond length is practically independent of the angle of rotation of the NO_2 group about the C—N bond. The same appreciable pyramidal character of the bonds formed by the amine nitrogen atom in pyrroles does not change in the N—N bond length.

In complex compounds containing a "pure" donor—acceptor bond involving the nitrogen atom, the stereochemistry of the donor and acceptor fragments is consistent with Gillespie's ideas. The almost square structure of the planar four-membered rings in the dimeric complexes of metal amino-derivatives is difficult to explain, however, because of the differences in the elastic constants of the valence angles at the atoms of nitrogen and the acceptor metal.

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