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The Molecular Geometry of Nitro-compounds

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A systematic account is given of data on the molecular geometries of approximately 300 nitro-compounds obtained for the vapours by gas electron diffraction and microwave spectroscopy and for the crystalline phases by X-ray diffraction. Certain rules have been formulated for the variation of the geometrical parameters of the molecules in the principal classes of nitro-compounds: inorganic, aliphatic, alicyclic, and aromatic nitro-compounds, nitroamines, and salts and complexes of nitro-alkanes and aromatic nitro-compounds.
The bibliography includes 181 references.

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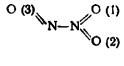
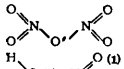
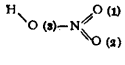
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I. INTRODUCTION

Nitro-compounds constitute a class of compounds which is important for practical and theoretical chemistry. The nitrogen atom in the NO_2 group has a specific valence state. From the standpoint of the classical theory of chemical structures, the valence of the nitrogen atom in the nitro-group $-N\begin{smallmatrix}O\\O\end{smallmatrix}$ is five, but approximate quantum-chemical ideas do not allow an increase of the valence of the nitrogen atom above four. On the basis of the concept that the nitrogen atom is quadrivalent, pronounced electron-accepting properties of the nitro-group have been postulated.

Analysis of data on the geometrical structure of the molecules is particularly important for the determination of the relation between the chemical structure and physicochemical properties of nitro-compounds. Numerous studies on these compounds have now been made by different methods: by gas electron diffraction (GE) and microwave spectroscopy (MW) for the vapours of the substances and by X-ray diffraction (XD) and neutron diffraction (to a much lesser extent) for the crystalline phase. Unfortunately, the results are not uniformly distributed with respect to different classes of compounds. The majority of data refer to the structures of aromatic nitro-compounds in the crystalline phase; there have been few electron diffraction and microwave studies on the free molecules in the gas phase.

Table 1. Geometrical parameters of inorganic nitro-compounds in the gas phase.

Structural formula	Symmetry	Parameters of nitro-group			Other bonds and valence angles	Method	Parameter	References
		r(N=O), Å	∠ONO, deg	r(O...O), Å				
	C_{2v}	1.1934(10) 1.202(3)	134.07(1.6) 134.0(1.3)	2.198 2.213	—	MW GE	r_a r_a	[1] [2]
	C_s	NO(1) 1.202(6) NO(2) 1.217(7)	129.8(1.1)	2.190	r(NO(3))=1.142(4) Å r(NN)=1.864(7) Å ∠O(3)NN=105.1(0.1)° ∠NNO(1)=112.7(0.7)° ∠NNO(2)=117.5(0.4)°	MW	r_s	[4]
	D_{2h}	1.190(2)	135.4(0.6)	2.201	r(NN)=1.782(8) Å	GE	r_a	[5]
	—	1.21(1)	134(5)		r(NO′)=1.46(2) Å, ∠NO′N95(30)°	GE		[6]
	C_s	NO(1) 1.211(5) NO(2) 1.199(5)	130.2(0.5)	2.184	r(NO(3))=1.406(5) Å r(OH)=0.964(10) Å ∠O(1)NO(3)=115.9(0.5)° ∠O(2)NO(3)=113.9(0.5)°	MW	r_s	[7]
	C_{2v}	1.180(5)	136.0(1.5)	2.188	r(NF)=1.467(15) Å	MW	r_s	[8]
	C_{2v}	1.202(20)	130.6(2.0)	2.181	r(NCl)=1.840(20) Å	MW	r_0	[9]
	C_s	1.206	130.1(0.5)	2.185	r(NN)=1.427 (3) Å r(NH)=1.005(15) Å ∠HNH=115.2(3.0)° ∠Φ=51.8(1.5)°	MW	r_0	[10]

Note. The errors of the determination of the parameters, referring to the last significant figures, are given in brackets, for example 1.190(2) Å = 1.190 ± 0.002 Å and 130.2(0.5)° = 130.2 ± 0.5°. For the differences between the types of the parameters r_a, r_0, and r_s due to vibrational effects and usually amounting to <0.01 Å, see, for example, Vilkov et al.[3] The bond length r(N=O) = 1.206 Å in NH_2NO_2 was fixed and was not varied in refining the parameters; Φ is the angle between the NH_2 and NNO_2 planes.

The task of the analysis of the molecular structure consisted in the determination of the rules governing the variation of the geometries of the groups CNO_2 (*C*-nitro-compounds), NNO_2 (*N*-nitroamines), and ONO_2 (*O*-nitro-compounds) as a function of the class of compound and the nature of the atoms and groups of atoms linked to the above groups. On the other hand, it is necessary to elucidate the influence of the NO_2 group on the neighbouring groups of atoms in the molecules of nitro-compounds. The molecular confirmation and the nature of the internal rotation of the nitro-group are important.

The review includes literature data up to 1978 inclusive and the results of a few studies in 1979. Since virtually all the data for the crystal structures published up to 1971 have been included in handbooks, references to the latter are given.

II. GEOMETRICAL STRUCTURE OF THE MOLECULES OF NITRO-COMPOUNDS IN THE GAS PHASE

1. Inorganic Nitro-Compounds

The determination of gas-phase structural data for inorganic nitro-compounds such as nitrogen oxides, nitric acid, and nitryl halides is associated with considerable experimental difficulties. As apparatus and experimental techniques have improved, the molecular geometries of these compounds have been reinvestigated. The results of the latest electron diffraction and microwave studies are presented in Table 1.

The N=O bond length in the nitro-group is almost constant and amounts to 1.20 Å on average. The ONO valence angle varies within wide limits, from 130° to 136°. The smallest value of r(N=O) and the greatest value of ∠ONO have been found for the NO_2F molecule, which is attributed to the high electronegativity of the fluorine atom[8]. We may note that, despite certain differences in the N=O bond lengths and ONO valence angles, the distance between the oxygen atoms in the nitro-group remains constant to within 0.02 Å.

The N_2O_3 and N_2O_4 molecules are characterised by unusually low N–N bonds, whose length exceeds by 0.3 Å the lengths of the corresponding bonds in hydrazine and its derivatives[3]. The nature of the N–N bond in these molecules has been discussed, for example, in a review[11]. The N–F and N–Cl bond lengths in the NO_2F and NO_2Cl molecules are greater than these bond lengths in NF_3 (1.36 Å) and NCl_3 (1.77 Å).

The molecules of the compounds presented in Table 1 are planar with the exception of N_2O_5 and NH_2NO_2. The conformation of the N_2O_5 molecule has not been reliably determined owing to the rotational movement of the nitro-group. In nitramide the amino-nitrogen atom has a pyramidal configuration of the bonds. In the determination of the geometry of this compound from the microwave spectrum[10], the N=O bond length, which is an important parameter, was assumed†. It has been shown[12] that another set of parameters, in which r(N=O) = 1.232 Å and r(N–N) = 1.381 Å, is consistent with the moments of inertia obtained[10]; this is consistent with the corresponding parameters of nitroamines (see Table 4 below).

2. Organic Nitro-Compounds

The majority of the molecular structures of simple aliphatic and aromatic nitro-compounds as well as nitroamines were investigated in the gas phase for the first time in the course of the last decade. The earlier data for the molecular geometries of CH_3NO_2, CH_3ONO_2, and $C(NO_2)_4$ have also been

Table 2. Principal geometrical parameters of the molecules of aliphatic nitro-compounds in the gas phase (X = C, F, Cl, or Br).

Compound	r(N=O), Å	r(C–N), Å	r(C–X), Å	∠ONO, deg	∠XCN, deg	Conformation	Method	Parameter	Refs.
CH_3NO_2	1.224 (5)	1.489 (5)	—	125.3(0.5)	—	free rot.	MW	r_a	[13]
CH_2ClNO_2	1.228 (2)	1.506 (9)	1.765 (9)	129.0 (1.5)	114.0 (1.0)	hindered rot.	GE	r_a	[14, 15]
CF_3NO_2	[1.22]	1.490	[1.325]	[127]	[109]	free rot.	MW	r_0	[16]
CF_3NO_2	1.21 (1)	1.56 (2)	1.325 (5)	132 (2)	109 (1)	hindered rot.	GE	r_a	[17]
CCl_3NO_2	1.190 (6)	1.594 (20)	1.726 (5)	131.7 (2.6)	106.0 (1.1)	hindered rot.	GE	r_a	[18]
CBr_3NO_2	1.22 (1)	1.59 (2)	1.92 (1)	134 (3)	208.3 (2.5)	hindered rot.	GE	r_a	[17]
$C_2H_5NO_2$	1.213 (3)	1.505 (3)	[1.540]	[134]	—	C_s	MW	r_0	[19]
$CH_2{=}CHNO_2$	1.220 (6), 1.234 (4)	1.471 (3)	1.322 (5)	126.0 (0.3)	121.2 (0.2)	C_s, planar	MW	r_s	[20]
▷—NO_2	1.213 (21)	1.488 (20)	[1.511]	[130]	—	C_s, bisector type	MW	r_0	[21]
$CCl_2(NO_2)_2$	1.224 (4)	1.506 (12)	1.757 (8)	124.9 (1.1)	109.7 (0.7)	C_2; φ=74(3)°	GE	r_a	[22]
$CH(NO_2)_3$	1.219 (3)	1.505 (5)	—	128.6 (1.0)	—	C_3; φ=26(1)°	GE	r_a	[23]
$CCl(NO_2)_3$	1.213 (3)	1.513 (3)	1.712 (4)	128.3 (0.6)	112.1 (0.5)	C_3; φ=49(1)°	GE	r_a	[23]
$CBr(NO_2)_3$	1.214 (3)	1.514 (6)	1.885 (9)	132.5 (2.0)	111.3 (1.0)	C_3; φ=49(1)°	GE	r_a	[23]
$C(NO_2)_4$	1.218 (2)	1.526 (6)	—	129.3 (1.0)	—	S_4; φ=47(4)°	GE	r_a	[24]

Note. The assumed values of the parameters are given in square brackets; φ is the angle of rotation of the NO_2 group about the C–N bond; φ = 0° for the coplanar disposition of the nitro-groups in $CCl_2(NO_2)_2$ and $C(NO_2)_4$ (D_{2d}) and for the planar arrangement of the XCNO atoms in $CX(NO_2)_3$.

† Here and henceforth the term "assumed" implies that the parameter was fixed and was not varied in the minimisation process whereby the parameters were refined.

revised. The principal structural parameters are presented in Table 2. A fairly detailed discussion of the molecular structures of organic nitro-compounds in the gas phase can be found in a book[3] and in a review[25]. We shall therefore confine ourselves to only a brief consideration of the principal characteristics of their geometrical structures.

The study of the molecular structures of aliphatic nitro-compounds (Table 2) has shown that the parameters of the nitro-group depend little on the substituent. In particular, the mutual influence of several nitro-groups in polynitroalkanes is weakly reflected in the geometry of these groups. The constancy of the N=O bond length (the average value is 1.22 Å) is particularly characteristic. The ONO angle is on average 129° with a maximum deviation of ±4° (we may note that angles exceeding 130° are quoted with large errors). The minimum value ∠ONO = 125° has been found for nitromethane and dichlorodinitromethane.

The C–N bond lengths in nitroalkanes are in the range 1.49–1.53 Å. Halogenopicrins, whose structure is discussed below, are an exception. There is a tendency towards an increase of r(C–N) with increase of the number of nitro-groups:

Compound	CH_3NO_2	$CH(NO_2)_3$	$C(NO_2)_4$
r(C–N), Å	1.489 (5)	1.505 (5)	1.526 (6) . #

A characteristic geometrical feature of the CNO_2 group is its planar structure[13,16,19,20].

Under the influence of nitro-groups, the lengths of the C–Cl and C–Br bonds adjoining them diminish, which is particularly notable in trinitro-compounds. The bond lengths r(C–Cl) = 1.712(4) Å in $CCl(NO_2)_3$ and r(C–Br) = 1.885(9) Å in $CBr(NO_2)_3$ are the shortest for bonds of the type $\geq$C–X (X = Cl or Br) and are virtually identical with the corresponding bond lengths in the vinyl derivatives.

Halogenopicrins CX_3NO_2 (X = F, Cl, or Br), the electron diffraction data for which conflict with the results of microwave studies on CH_3NO_2 [13,27] and CF_3NO_2,[16] occupy a special place among the mononitroalkanes presented in Table 2. Electron diffraction study of halogenopicrin molecules yielded unusually high C–N bond lengths (up to 1.59 Å), demonstrated hindered rotation about this bond with a barrier of approximately 3 kcal mol^{-1}, and revealed a slight deviation from the planar structure of the CNO_2 groups, leading to a preferred staggered conformation. According to microwave data for CF_3NO_2 (and also CH_3NO_2), the C–N bond length is 1.49 Å, the rotation about this bond is free, and the CNO_2 group is planar. Analysis of electron diffraction data, carried out by the compilers of a handbook[28], led them to the conclusion that these had been obtained with a lower accuracy than indicated by the authors[17,18] [for example, the real error of the determination of r(C–N) is 0.06 Å] and that the barrier to rotation is probably too high. Thus the problem of the molecular structure of halogenopicrins cannot be regarded as ultimately solved.

The molecules of nitroethane, nitroethylene, and nitrocyclopropane have the C_S symmetry. The NO_2 group in nitroethane is in the same plane as the C–N and C–C bonds, and the four hydrogen atoms are arranged symmetrically above and below this plane. The nitroethylene molecule is also planar. Only a bisectorial conformer has been found for nitrocyclopropane in which the plane of the nitro-group is at right angles to the plane of the three-membered ring. The barrier to rotation about the C–N bond in the nitrocyclopropane molecule has been estimated as 1100 ± 500 cm^{-1} or 3.3 ± 1.5 kcal mol^{-1}.

A characteristic feature of the conformation of polynitroalkane molecules in the gas phase is that the angles of rotation of the nitro-groups relative to the N–C–X plane (X = H, Cl, Br, or N) differ from 0° (Table 2). The non-bonded O...Hal and N...O distances are reduced compared with the sum of the van der Waals radii, while the O...O distances are normal. Theoretical calculations of the molecular conformations of trinitro-compounds[29] and tetranitromethane[30] on the basis of a mechanical model agree satisfactorily with experiment; such agreement has not been obtained for dichlorodinitromethane[29].

The geometrical parameters of aromatic nitro-compounds are presented in Table 3. Comparison of the C–N bond lengths and ONO angles in aromatic and aliphatic nitro-compounds shows that as a rule both these parameters are smaller for benzene derivatives than for saturated aliphatic compounds. On the other hand, the equality of the r(C–N) in aliphatic and aromatic nitro-compounds has been noted in a number of monographs (see, for example, Feuer[36]) on the basis of old experimental data, which is difficult to reconcile with the ideas concerning their electronic structure.

The principal conclusion which follows from the study of the molecular structures of aromatic nitro-compounds in the gas phase is that the geometry of their benzene ring is altered. Thus the average C...C bond length§ in $C_6H_5NO_2$, *sym*-$C_6H_3(NO)_3$, *p*-$C_6H_4(NO_2)_2$, and *p*-$ClC_6H_4NO_2$ is smaller than in benzene [r_g = 1.399(1) Å] [3] and is almost independent of the number of nitro-groups. The $CC_{NO_2}C$ valence angle at the carbon atom linked to the nitro-group is greater than 120° in all the compounds listed in Table 3 except *o*-$C_6H_4(NO_2)_2$.

It has been shown in relation to *p*-nitroaniline and *p*-chloronitrobenzene that the nitro-group shortens the C–X (X = Cl or NH_2) bonds, while the CC_XC valence angle hardly changes:

Compound	$C_6H_5NH_2$ [3]	$NH_2C_6H_4NO_2$ [35]	C_6H_5Cl [37]	$ClC_6H_4NO_2$ [34]
r(C–X), Å	1,402 (2)	1,367 (17)	1,737 (5)	1,707 (4)
∠CC_XC, deg	119,5 (2)	119,8 (1,7)	121,7 (0.6)	120,5 (0,6)

Note. The numbers in square brackets denote references (Ed. of Translation).

The *o*-dinitrobenzene molecule, in which there is appreciable steric hindrance, is non-planar and its conformation is characterised not only by the rotation of the nitro-group but also by the deviation of the C–N bonds by 3.6° from the direction of the bisector and by their displacement from the plane of the ring (by approximately 1°) (which fully agrees with a conformational calculation[38]). The non-planar conformations of the other compounds in Table 3, determined by electron diffraction, is associated with the torsional vibrations of the nitro-groups. Allowance for these vibrations leads to a planar equilibrium model with a barrier to rotation $V_2 \cong 5$ kcal mol^{-1}.[39]

In analysing the structural data for *N*-nitroamines (Table 4), it is important to elucidate the dependence of the change in the N–N bond length and in the molecular configuration on

The value r(C–N) = 1.47 Å was quoted in an early electron diffraction study[26]. The difference of 0.05 Å from the result of a reinvestigation[24] presented here can be associated with the inaccuracy of the earlier visual method.

§ The bond lengths in the benzene rings of the molecules investigated were not found to be unequal, although models with different bond lengths have been considered in structural analysis.

Table 3. Principal geometrical parameters of aromatic nitro-compounds in the gas phase.

Compound	r(N=O), Å	r(C–N), Å	r(C...C), Å	∠ONO, deg	∠$CC_{NO_2}C$, deg	φ_{NO_2}, deg	References
$C_6H_5NO_2$	1.226	1.492	1.391	124.4	125.0	0	[31, 32]
o-$C_6H_4(NO_2)_2$	1.224 (2)	1.475 (12)	1.397 (2)	124.9 (0.5)	120.4 (1.2)	31.1 (1.8)	[33]
p-$C_6H_4(NO_2)_2$	1.221 (2)	1.463 (10)	1.392 (2)	125.8 (0.5)	122.9 (0.9)	18.5 (4.1)	[33]
sym-$C_6H_3(NO_2)_3$	1.224 (2)	1.475 (5)	1.388 (2)	125.7 (0.5)	123.2 (0.9)	21.0 (2.3)	[33]
p-$ClC_6H_4NO_2$	1.237 (3)	1.469 (13)	1.388 (1)	123.0 (0.9)	122.6 (1.1)	18.9 (5.3)	[34]
p-$H_2NC_6H_4NO_2$	1.225 (2)	1.470 (11)	1.402 (3)	124.7 (0.7)	122.8 (1.4)	17.4 (7.4)	[35]

Note. Nitrobenzene was investigated by microwave spectroscopy (parameters r_S); the remaining compounds were studied by electron diffraction (parameters r_g); ϕ is the angle of rotation of the NO_2 group about the C–N bond.

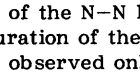
Table 4. Principal parameters of the molecules of *N*-methylnitroamines having the general formula  in the gas phase.

X	r(N=O), Å	r(N–N), Å	r(C–N), Å	∠ONO*	∠CNN*	∠CNX*	∠CNNO*	References
H	1.228 (3)	1.381 (6)	1.452 (6)	125.3 (1.0)	109.0 (1.3)	119 (1)	28	[12]
CH_3	1.223 (2)	1.382 (3)	1.460 (3)	130.4 (1.5)	116.2 (0.3)	127.6 (0.6)	0	[40]
CH_2Cl*	1.220 (3)	1.426 (10) ***		123.5 (0.5)	116.2 (0.5)	127.5 (0.5)	35	[41]
Cl**	1.209 (2)	1.469 (5)	1.478 (5)	128.5 (0.9)	112.9 (1.5)	115.0 (1.2)	27	[12]
NO_2	1.231 (3)	1.480 (5)	1.494 (6)	132 (1)	107.5 (1.1)	107.5 (1.1)	28	[42]

*r(C–Cl) = 1.790(7) Å, ∠NCCl = 112.3(0.8)°.
**r(N–Cl) = 1.720(4) Å, ∠ClNN = 108.4(1.3)°; the dihedral ClNNO angle is 24.4°.
***The average value is quoted.

the substituents at the amino-nitrogen atom. It was found that the replacement of the CH_3 group or a hydrogen atom in methylamines by a chlorine atom or the NO_2 group leads to a marked increase of the N–N length (by approximately 0.1 Å). A planar configuration of the bonds involving the amino-nitrogen atom is observed only in the $(CH_3)_2NNO_2$ and $(CH_2Cl)CH_3NNO_2$ molecules. Moreover, whereas the dimethylnitramine molecule is planar overall†, the nitro-group in the *N*-chloromethyl-*N*-methylnitroamine molecule has been rotated by 35°. In other *N*-substituted nitroamines and nitramide (Table 1) the amino-nitrogen atom has a pyramidal configuration of the bonds. This leads to the conclusion that the configuration of the amino-nitrogen bonds depends only on the atoms and groups of atoms linked directly to the nitrogen atom. Overall, greater differences between the structural parameters are observed for *N*-nitroamines than for *C*-nitro-compounds. The complex geometrical relations for nitroamines require further study.

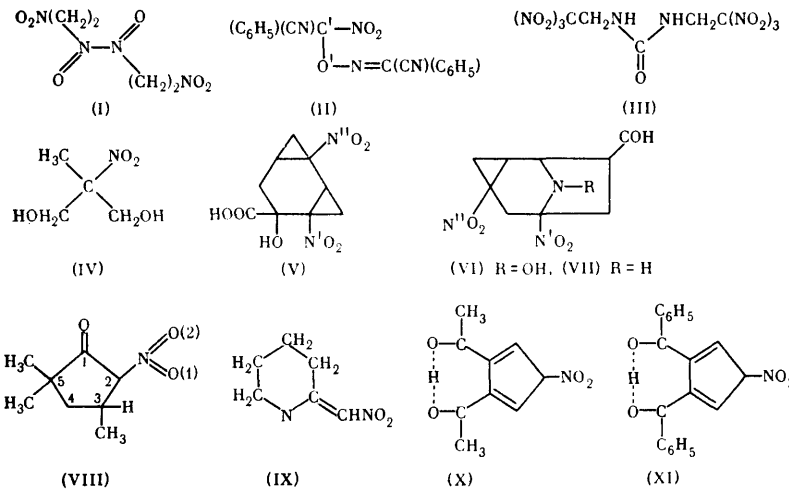
† Here and henceforth the term "assumed" implies that the parameter was fixed and was not varied in the minimisation process whereby the parameters were refined.

The molecular structures of *O*-nitro-compounds have been hardly investigated in the gas phase. Fairly reliable structural data have been obtained only for methyl nitrate[43]. The  molecule has the C_s symmetry and a planar skeleton with the following parameters: r(N–O) = 1.205(5) Å, r(N–O′) = 1.402(5) Å, r(C–O′) = 1.437(5) Å, ∠O′NO = 118.1(0.3)° (*cis*), ∠O′NO = 112.4(0.3)° (*trans*), and ∠CO′N = 112.7(0.3)°. Thus the parameters of the nitro-group are close to the corresponding parameters of aliphatic nitro-compounds and nitroamines.

III. THE GEOMETRICAL STRUCTURE OF THE MOLECULES OF NITRO-COMPOUNDS IN THE CRYSTAL

1. Aliphatic and Alicyclic *C*-Nitro-compounds

There have been only a few studies of aliphatic and alicyclic nitro-compounds by X-ray diffraction and their accuracy has been low in a number of instances. The structures whose parameters have been obtained with satisfactory accuracy, are presented in Table 5.



Owing to the scatter of the bond lengths and valence angles, it is difficult to compare them with the analogous compounds in the gas phase. Averaging of the geometrical parameters of the CNO_2 groups yields the following values: $r(N=O)$ = 1.21 Å, $r(C-N)$ = 1.50 Å, and ∠ONO = 124°. The average N=O and C–N internuclear distances obtained agree, within the limits of the errors, with the average values of the same distances in the compounds investigated in the gas phase; the ONO angle is somewhat smaller.

Table 5. Geometrical parameters of the CNO_2 group in a series of aliphatic and alicyclic nitro-compounds in the crystalline phase.

Compound	r(N=O), Å	r(C–N), Å	∠ONO,*	∠NCC,*	Refs.
(I)	1.205(5) * 1.198(4)	1.485 (5)*	123.2 (0.4)	112.3 (0.4)	[44]
(II)	1.165(7) 1.126(6)	1.617 (6)	130.0 (0.5)	107.9 (0.3)	[45]
(III)	1.210(15)	1.510 (15)	127.2 (1.1)	111.8—113.3**	[46]
(IV)	1.210(4) 1.200(4)	1.506 (4)	122.3 (0.3)	105.6—108.9	[47]
(V)	N′O_2 1.232(4); 1.217(4) N″O_2 1.224(4)	1.486 (4) 1.476 (4)	122.7 (0.3) 123.4 (0.3)	112.6—113.3 113.4—115.4	[48]
(VI), (VII)***	N′O_2 1.209(4) N″O_2 1.219(5)	1.528 (3) 1.482 (3)	124.0 (0.2) 122.8 (0.2)	108.0—110.8 114.1—115.7	[49]
(VIII)	1.222(5) 1.197(5)	1.486 (4)	123.7 (0.3)	109.5 (0.2) 114.0 (0.2)	[50]
(IX)	1.246(7) 1.262(7)	1.362 (8)	117.7 (0.6)	126.0 (0.7)	[51]
(X)	1.226(3)	1.432 (3)	122.9 (0.2)	124.4 (0.2)	[52]
(XI)	1.230(2)	1.433 (4)	123.6 (0.2)	124.5 (0.2)	[52]

Note. The values of $r(N=O)$ in the NO_2 group are given as independent parameters which can differ both within the same group and in different groups. When the differences are small, the average value is quoted; different nitro-groups are designated by primes.

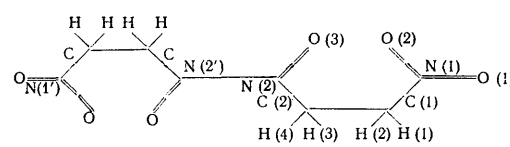
*$r(N=O)$ = 1.262(4) Å in the nitroso-group; $r(C-N_{nitroso})$ = 1.470(5) Å.

**The $N_{NO_2}CN_{NO_2}$ are 107.2(0.8)°, 107.1(0.8)°, and 104.8(0.8)°.

***The parameters of compounds (VI) and (VII) agree within the limits of the errors and average values are quoted here.

In two instances there are considerable deviations of the C–N bond lengths from the mean. An unusually long $C-NO_2$ bond [1.617(6) Å, cf. CX_3NO_2] has been found in the *o*-(phenylcyanonitromethyl)benzoylcyanoxime molecule[45], which led the authors to the conclusion that the $C-NO_2$ bond is weakened, which was confirmed by mass-spectrometric data. The $C-NO_2$ bond in 2-(nitromethylene)piperidine[51], where the nitro-group is linked to a carbon atom of the type $=C\langle$, is shortened to 1.362(8) Å, which is smaller by 0.1 Å than in aromatic nitro-compounds. The ONO angle also is unusually small [117.7(0.6)° (the deviations of the parameters of the CNO_2 groups are not discussed by Kokkou and Rentzeperis[45])]. The nitro-group is in the *cis*-position relative to the nitrogen atom of the ring.

We shall consider certain conformational features of the compounds investigated. The dimer of 2-nitronitrosoethane[44]



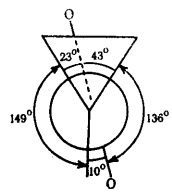
has the *trans*-configuration with the centre of symmetry in the middle of the N–N bond. In the monomeric fragments a staggered conformation is observed with projection of the C(1)–N(1) bond approximately on the bisector of the H(4)C(2)N(2) bond. This conformation is stabilised (according to Ref.44) by intramolecular interactions between the negatively charged oxygen atom O(2) of the nitro-group and the positively charged nitrogen atom (2) and by similar interactions between N(1) and O(3). The N(2)...O(2), N(1)...O(3), O(1)...O(3), and N(1)...N(2) distances are greater than the sums of the van der Waals radii. The N–N bond length [1.304(4) Å] agrees with the value found for other nitroso-compounds, for example, *cis*-nitrosomethane (1.31 Å),[54] *p*-bromonitrosobenzene (1.31 Å),[56] and potassium dinitrososulphite (1.30 Å).[56]

The plane of the NO_2 group in *O*-(phenylcyanonitromethyl)-benzenecyanoxime[45] makes a dihedral angle of 83° with the plane of the main atomic chain C′–O′–N=C and a 75° angle with the plane of the benzene ring attached to the C′ atom.

The conformations of the $C-C(NO_2)_3$ fragments in compounds such as *N*,*N*′-bis(β,β,β-trinitroethylurea[46] and *N*-(2,2,2-trinitroisopropyl)amides of chloro- and bromoacetic acids[53] are on the whole similar to the conformations

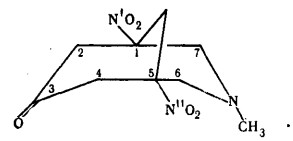
of the trinitro-compounds investigated in the gas phase. Thus the nitro-groups in the $CH_2XC(O)NHC(CH_3)C(NO_2)_3$ molecules[53] form a propeller" configuration. A relative disposition of the nitro-groups in the $OC[NHCH_2C(NO_2)_3]_2$ molecule has been indicated such that the three N...O distances between the nitrogen and oxygen atoms of neighbouring nitro-groups are reduced to 2.56 Å compared with the sum of the van der Waals radii (2.80 Å). Other N...O and O...O distances are equal to or greater than the sum of the van der Waals radii.

For alicyclic nitro-compounds, it is important to elucidate the disposition of the nitro-group relative to the ring. The determination of the conformation of the nitrocyclopropane fragment in the 6-hydroxymethylene-1,3-dinitro-*N*-oxy-3,4-methanonortropane molecule[49] yielded the results illustrated below on a Newman projection:



The same conformation of the nitrocyclopropane fragment has been found in 6,6-dibromo-2,3 : 4,5-dimethano-2,4-dinitrocyclohexanone[54].

The relative orientations of the nitro-group and the five-membered ring in the 3,5,5-trimethyl-2-nitrocyclopentanone molecule[50] are determined by the CCNO dihedral angles, which are approximately 60°. Accordingly, the angle between the planes of the ring and of the nitro-group is 95°, i.e. the nitro-group is almost perpendicular to the cyclopentane ring. The ring has the form of a slightly twisted "half-chair" with C_1 symmetry. The nitro-group and the nearest CH_3 group are in the *trans*-positions. Different orientations of the nitro-groups relative to the bicyclononane skeleton have been observed in 1,5-dinitro-3-azabicyclo[3,3,1]nonan-7-one,[55] for which two modifications have been investigated—A (space group $P2_1/c$) and B (space group $Pccn$).



The $N'O_2$ group virtually eclipses the C(1)–C(2) bond in A and B, while the other nitro-group is perpendicular to the C(5)–C(4) bond in A and eclipses the C(5)–C(6) bond in B. Thus the molecules of modifications A and B are conformational isomers.

Table 5 also presents data for the molecules of two derivatives of 5-nitrocyclopentadiene[52]. The $C-NO_2$ bond lengths in these molecules (1.43 Å) are somewhat smaller than in nitrobenzenes (1.47 Å); the remaining parameters of the CNO_2 group are closer to the parameters of aromatic rather than aliphatic nitro-compounds. In the five-membered ring the C(3)–C(4) bond length (1.446 Å) is similar to that of the $=C-C=$ bond in cyclo-octatetraene[3], while the remaining bond lengths are the same within the limits of the errors (the average bond length is 1.396 Å). The enolic hydrogen atom is midway between the two oxygen atoms and forms a short symmetrical intramolecular O...H...O bond, the O...O distance being 2.43–2.45 Å. A fairly complex picture is observed for the anions of aliphatic nitro-compounds. The structure of mononitrocarbanions has been investigated[56–58]. The parameters of the CNO_2 group in these compounds, i.e. $r(N=O)$ = 1.25–1.32 Å, $r(C-N)$ = 1.37–1.39 Å, and ∠ONO = 117–121°, are significantly altered compared with the values found for neutral nitro-compounds, which can be attributed to the distribution of the charge of the anion[57].

The nitroacetate dianion $[OOC-CH-NO_2]^{2-}$ has a planar structure[56]. The atoms of the phenylnitroacetonitrile anion[57]

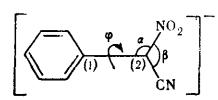


Table 6. Structural parameters of certain carbanions of the type $[R-C(NO_2)_2]$.

R	Cation	C–N	N=O	∠NCN	∠CNO	∠ONO	φ	τ	Refs
—CN	K^+	1.394	1.238	123,7	122,5	122,0	7; —7	~0	[59]
—CN	Rb^+	1.377	1.240	125,2	121,5	121.0	2.7; —5,5	~0	[60]
$-C(NO_2)_2$	K^+	1.390	1.245	121	121	120	13; 6.3	63	[61]
$-C(NO_2)_2$	Rb^+	1.380	1.243	122.5	122.6	120,5	4.1; 6.1	68	[62]
$-CONH_2$	Rb^+	1.35	1.255	123	123.5	120.5	2; 5	79	[46]
$-CH=CHCONH_2$	K^+	1.389	1.248	120.0	122,5	119,5	0; 0	0	[61]
$-C(C\equiv N)(CH_3)_2$	K^+	1.43	1.27	119	121	119	0; 30	—	[64]
$-CH_2-C(NO_2)_2(CH_2)_2C(O)CH_3$	Rb^+	1.37	1.24	120	125	113	0; 4	~90	[44]
$-C_6H_5$	K^+	1.40	1.275	120	124	119	~10; ~10	62	[46]
$-C_6H_4Cl$	K^+	1.389	1.256	119,8	123,6	120,5	10; —7	71	[65]
$-C_6H_2(NO_2)_3$	Rb^+	1.38	1.24	122	121	118	0; 0	60	[66]
$-NO_2$	$N_2H_5^+$	1.391	1.231	124.3	120.4		—7; —8	71	[46]
$-NO_2$	$N_2H_5^+$	1.371	1.239	127.2	120.7		5, 3	74	[46]

Note. The average values of the bond lengths (Å) and valence angles (degrees) in the $C(NO_2)_2$ group are quoted; ϕ are the angles of rotation of the nitro-group; τ is the angle of rotation of planar $C(NO_2)_2$ groups about the C–C(N) bond. The accuracy of the determination of the bond lengths is to within not more than 0.02 Å and that of the angles is to within not more than 2°; the data for a series of salts, obtained with a lower accuracy, are not included in the Table. In the salt of *N*-methyl-α,α-nitroacetamide (R = $CONH_2$) one nitro-group is coplanar with the amide group, while the other forms an angle of 53° relative to the latter[63].

are located in virtually two planes—those of the cyanonitromethyl fragment and of the benzene ring. The angle of rotation of the benzene ring relative to the $O_2N-C-CN$ plane is 17°. The angle α is increased to 130(3)°, while the angle is compressed to 111(3)°. The O...C(1) distance (2.87 Å) is then reduced compared with the sum of the van der Waals radii. It has been noted[58] that the geometry of the anion $[O_2NC(CN)_2]^-$ is very sensitive to the environment (in the present instance owing to the coordination to the Ag^+ ions).

The structure of the salts of polynitro-compounds containing a carbanion of the type $[R-C(NO_2)_2]^-$, including the trinitromethyl anion $[C(NO_2)_3]^-$ (R = NO_2), has been studied in greatest detail (Table 6). The parameters of the $C(NO_2)_2$ group in the carbanion differ significantly from those for the usual aliphatic nitro-compounds. Thus the C–N bond length is smaller by approximately 0.1 Å than the usual value and the CNC angle is unusually large (>120°). Appreciable differences have been observed for r(N=O) and ∠CNO. In many instance the N=O bond lengths were found to be unequal within the same nitro-group (by up to 0.06 Å).

As a rule, the $C(NO_2)$ group is almost planar and the rotations of the NO_2 groups relative to the plane are small (up to approximately 10°). The shortest O...O distance between neighbouring nitro-groups is approximately 2.6 Å. The increase of the "inner" CNO angles compared with the "outer" angles by approximately 6° is consistent with the hypothesis that the oxygen atoms of the two nitro-groups repel one another. The influence of the bulky substituent $(CH_3)_2CCN$, incapable of conjugation, on the deviation of the nitro-groups from coplanarity has been examined in relation to the anion of 2,2-dimethyl-1,1-dinitropropionitrile[64]. One of the nitro-groups has been rotated by the angle $\phi = 30°$ relative to the C–N bond, which the authors[64] attributed to the mutual repulsion of the oxygen atoms of this nitro-group and the atoms of the methyl group.

Studies of the salts $X[C(NO_2)_3]$ (X = N_2H_5,[46] K,[67] Rb,[61] or Cs [68]) have shown that the nitro-groups of the trinitromethyl anion are non-equivalent, two being located in virtually the same plane, while the third forms an angle relative to this plane.

General analysis of structural data for the anions of aliphatic nitro-compounds leads to the conclusion that the structure of the anion in the crystalline state is determined by a number of factors, among which crystal packing, intermolecular steric interactions, coordination, etc. play a significant role. It is noteworthy that unfortunately the accuracy of many studies of the salts of nitro-compounds has been low.

2. Aromatic Nitro-Compounds

Aromatic nitro-compounds constitute the largest group of nitro-compounds whose structure is now known (Table 7). It has been noted that, under the influence of the nitro-group, the geometry of the benzene ring changes, namely the inner angle at the carbon atom, to which the nitro-group is attached, as a rule exceeds 120°. This has been accounted for by the electron-accepting properties of the NO_2 group, which alter the hybridisation of the carbon atom[107]. The influence of various functional groups, including the nitro-group, on the geometry of the benzene ring has been most thoroughly examined by Domenicano et al.[108] and by Zvonkova[109] on the basis of a statistical analysis of extensive experimental data.

The method involving the statistical treatment of experimental data has been applied also by the authors of the present review to the analysis of parameters of aromatic nitro-compounds such as $r(C\cdots C)$ and $\angle CC_{NO_2}C$ in the benzene ring and the parameters of the CNO_2 group, i.e. r(N=O), $r(C-NO_2)$, and ∠ONO.[110] When the number of structural data is large, this approach can reveal the fundamental characteristics of the geometrical structure of the class of compounds under consideration.

In connection with the problem of the mutual influence of atoms and groups of atoms in molecules, nitro-compounds containing the amino-group or a chlorine atom as substituents, the data for which are more numerous than those for other substituted nitro-compounds, have been of special interest. Accordingly statistical analysis has been performed for three groups of compounds: group I—compounds which do not contain the NH_2 group or a Cl atom as substituents; group II—nitro-compounds with one or several amino-groups; group III—nitro-compounds with one or several chlorine atoms. The results of the statistical treatment, presented in Table 7, have led to the following findings.

Table 7. The weighted-mean geometrical parameters of aromatic nitro-compounds.

n	$r(C\cdots C)$, Å	$r(C-NO_2)$, Å	$r(C-X)$, Å	r(N=O), Å	$\angle CC_{NO_2}C$,°	$\angle CC_XC$,°	∠ONO,°
Group I—aromatic nitro-compounds							
1	1.384 (1)	1.467 (2)	—	1.217 (1)	122.5 (0.1)		123.1 (0.1)
2	1.383 (2)	1.473 (1)	—	1.221 (1)	123.1 (0.1)	—	124.7 (0 2)
3	1.385 (2)	1.474 (1)	—	1.218 (1)	123.3 (0.1)	—	124.8 (0.1)
Mean	1.384 (1)	1.473 (1)	—	1.218 (1)	123.2 (0.1)	—	124.5 (0.1)
Group II—aromatic nitroamines							
1	1.393 (3)	1.462 (6)	1.371 (7)	1.224 (3)	122.7 (0.5)	118.5(0.5)	122.7 (0.4)
2	1.395 (7)	1.451 (8)	1.346 (16)	1.225 (4)	122.7 (0.9)	113.6(1.0)	122.8 (0.3)
3	1.402 (4)	1.470 (4)	1.322 (7)	1.231 (3)	123.0 (0.4)	116.5(0 3)	120.9 (0.9)
Mean	1.399 (2)	1.464 (4)	—	1.228 (2)	122.8 (0.3)	116.8(0.6)	121.9 (0.4)
Group III—chloronitrobenzenes							
1	1.388 (4)	1.452 (2)	1.744 (7)	1.219 (4)	122.0 (0.3)	121.4 (0.5)	122.6 (1.1)
2	1.385 (7)	1.466 (6)	1.721 (7)	1.215 (8)	122.9 (0.2)	122.0 (0.4)	123.7 (0.3)
3	1.376 (3)	1.471 (2)	1.708 (3)	1.400 (4)	121.9 (0.3)	117.0 (0.2)	120.3 (0.3)
Mean	1.380 (2)	1.468 (2)	—	1.212 (4)	122.3 (0.2)	120.3 (0.8)	124.1 (0.3)

In compounds of group I the average $C\cdots C$ bond length is 1.384 Å and is independent of the number n of nitro-groups. A similar value $r(C\cdots C)$ = 1.380 Å has been observed for compounds of group III. The results of X-ray diffraction analysis do not permit a reliable conclusion concerning variation of the $C\cdots C$ bond in the benzene ring and the influence of nitro-groups, since the values of $r(C\cdots C)$ in crystalline benzene are subject to a considerable scatter: 1.378(3) Å without allowance for thermal corrections and 1.392(10) Å when the latter are taken into account[56]. Comparison with neutron diffraction data [$r(C\cdots C)$ = 1.393(7) Å] [54] indicates a slight shortening of the $C\cdots C$ bond under the influence of the nitro-groups. This conclusion follows more distinctly from the above electron-diffraction data for $C_6H_3(NO_2)_3$ in the gas phase.

It has been noted[111] that the average length of the $C\cdots C$ bonds adjoining the NO_2 group is smaller and that of the bonds adjoining the NH_2 groups is larger than in benzene. However, the average $C\cdots C$ bond length in aromatic nitroamines (group II) is the same as in benzene in the gas phase (1.399 Å).

The above observation—the increase of the inner angles in the benzene ring at the nitro-group—has been confirmed for compounds of all three groups. The angles in the benzene ring at the amino-group are less than 120° and those at

the chlorine atom are the same as in benzene within the limits of the errors.

Comparison of geometrical parameters such as $r(N=O)$, $r(C-NO_2)$, and ∠ONO shows that $r(C-NO_2)$ in compounds of group I is greater than in those of groups II and III; $r(N=O)$ and ∠ONO are similar for groups I and III and differ from the corresponding parameters for group II and in aromatic nitroamines there is a tendency towards an increase of the N=O bond length and a decrease of the ONO angle. There have been a number of studies where the authors attempted

Table 8. Geometrical parameters of the simplest derivatives of nitrobenzene, dinitrobenzene, and trinitrobenzene in the crystalline state.

Compound	$r(N=O)$, Å	$r(C-N)$, Å	∠ONO, deg	$\angle CCNO_2C$, deg	φ,°	Refs.
Compounds with one nitro-group						
$C_6H_5NO_2$	1.208 (14)	1.486 (20)	124	125	0	[56]
p-$O_2NC_6H_4CH_3$ [a]	1.243 (7)	1.482 (7)	122.8 (0.5)	122.7 (0.5)	3	[69]
o-$O_2NC_6H_4SO_2Cl$ [b]	1.223 (15)	1.455 (15)	125.5 (1.1)	119.8 (1.1)	57	[46]
o-$O_2NC_6H_4OH$ [c]	1.219 (7)	1.456 (7)	123.6 (0.5)	120.7 (0.5)	2	[71]
m-$O_2NC_6H_4OH$ [d]	1.217 (3)	1.477 (3)	123.4 (0.2)	123.6 (0.2)	0	[74]
p-$O_2NC_6H_4OH$ (α)	1.234 (6)	1.442 (6)	122.0 (0.4)	122.3 (0.4)	1,5	[54]
(β) [e]	1.242 (3)	1.450 (3)	122.8	120	8	[54]
p-$O_2NC_6H_4OC(O)CH_3$ [f]	1.215 (17)	1.459 (18)	123.2	121.5	3	[75]
o-$O_2NC_6H_4CHO$	1.230 (10)	1.468 (8)	125.0 (0.6)	123.0 (0.6)	27	[54]
syn-p-$O_2NC_6H_4CHNOH$ [g]	1.214 (8)	1.432 (9)	121.7 (0.6)	120.5 (0.7)	5	[78]
p-$O_2NC_6H_4C(O)CH_3$	1.220 (4)	1.466 (4)	123.3 (0.3)	121.7 (0.3)	4	[81]
o-$O_2NC_6H_4COOH$	1.219 (8)	1.466 (9)	123.6 (0.6)	124.3 (0.6)	55	[67]
m-$O_2NC_6H_4COOH$ (stable form)	1.236 (8)	1.479 (8)	123.7 (0.5)	123.7 (0.6)	22(A)[h], 5(B)	[82]
Ditto (Unstable form) [i]	1.211 (8)	1.467 (8)	122.9 (0.5)	122.6 (0.5)	3(A)[h]; 1(B)	[83]
p-$O_2NC_6H_4COOH$ [j]	1.222 (2)	1.476 (2)	124.2 (0.1)	123.3 (0.1)	14	[84]
p-$O_2NC_6H_4C(O)OC[C(CH_3)_3]_2$ [k]	1.223 (7)	1.468 (7)	123.6 (0.5)	122.8 (0.5)	0	[85]
o-$O_2NC_6H_4C(O)NH_2$	1.225 (8)	1.465 (8)	124.1	122.1	47	[90]
p-$O_2NC_6H_4C(O)NH_2$	1.223 (3)	1.468 (3)	123.1 (0.2)	122.6 (0.2)	8	[91]
p-$O_2NC_6H_4CN$	1.213 (10)	1.483 (10)	123.8 (1.0)	122.7 (1.0)	10	[92]
p-$O_2NC_6H_4NNN$ [l]	1.240 (15)	1.449 (19)	121.3 (1.2)	123.0 (1.3)	4	[54]
Compounds with two nitro-groups						
m-$C_6H_4(NO_2)_2$ [m]	1.248 (6)	1.493 (6)	125.8 (0.6)	123.6 (0.6)	13	[68]
p-$C_6H_4(NO_2)_2$	1.20 (1)	1.49	127	123	12	[54]
2,4-$(NO_2)_2C_6H_3OH$ [n]	1.224(5)	1.448 (5)	123.7 (0.4)	122.2 (0.4)	3; 5 [o]	[93]
2,6-$(NO_2)_2C_6H_3OH$	1.241 (9)	1.465 (9)	122.9 (0.6)	122.1 (0.6)	3; 13	[96]
3,5-$(NO_2)_2CH_3C_6H_2COOH$	1.225(8)	1.481 (9)	124.7 (0.6)	124.8 (0.5)	48; 39	[44]
3,5-$(NO_2)_2C_6H_3C(O)O(CH_2)_2C(CH_3)_3$ [p]	1.221	1.401	123.8	123.0	—	[97]
2,4-$(NO_2)_2C_6H_3CH_2SO_2C_6H_4CH_3$	1.208 (4)	1.480 (4)	124.5 (0.3)	122.5 (0.3)	35; 10	[102]
Compounds with three and more nitro-groups						
sym-$C_6H_3(NO_2)_3$	1.207 (10)	1.477 (10)	125.1 (0.7)	123.4 (0.7)	3;28;8 (A);10;10;5(B)	[103]
2,4,6-$(NO_2)_3C_6H(CH_3)_2$	1.218 (4)	1.477 (4)	125.1 (0.3)	124.8 (0.3)	75; 36	[104]
2,4,6-$(NO_2)_3C_6H_2Cl$ [q]	1.214 (6)	1.472 (6)	124.1	122.4	81; 13; 33	[105]
2,4,6-$(NO_2)_3C_6H_2OC_2H_5$	1.214 (10)	1.469 (8)	124.0 (0.6)	122.7 (0.6)	61; 3	[61]
$(NO_2)_3C_6H_2N{=}NC_6H_2(NO_2)_3$ [r]	(I) 1.221 (5)	1.480 (5)	125	123	50; 15; 39	[106]
	(II) 1.211 (5)	1.482 (5)	126	123	29:1;86;37;22;53	
$C_6(NO_2)_6$	1.23	1.45	125	120	53	[68]

[a] There are also structural data for nitromesitylene[56] and pentamethylnitrobenzene[70].

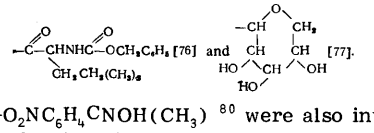
[b] The methyl ester of o-nitrobenzenesulphonic acid $O_2NC_6H_4SOCH_3$ was investigated[54].

[c] The structure of 4-chloro-2-nitrophenol was investigated[72,73].

[d] Monoclinic modification containing two independent molecules A and B in the unit cell. Their parameters do not differ within the limits of the errors. The average values are quoted here.

[e] Here α and β represent the stable and metastable modifications respectively.

[f] The p-nitrophenyl ethers $O_2NC_6H_4OR$ were investigated with the following groups R:



[76] and [77].

[g] The structures of $O_2NC_6H_4CClNOH$ [79] and p-$O_2NC_6H_4CNOH(CH_3)$ [80] were also investigated.

[h] The unit cell contains two independent molecules A and B and the average values of their bond lengths and valence angles are given.

[i] For structural data concerning 2-chloro-5-nitrobenzoic acid, see the relevant handbook[54].

[j] The structures of o- and p-nitroperoxybenzoic acids $O_2NC_6H_4C(O)OOH$ are given in handbooks[46,54].

[k] There are data for the structures of other nitrobenzoate esters of the type $O_2NC_6H_4C(O)OR$ with more complex groups R.[68,86-89]

[l] For data on o-, m-, and p-nitroanilines and their derivatives, see Table 9.

[m] For the structures of 1-chloro(bromo)-2,4-nitrobenzenes, see the relevant handbook[54].

[n] The chloro- and bromo-derivatives were investigated[94,95].

[o] Here and henceforth the angles of rotation of different nitro-groups are given; they are the same in m- and p-$C_6H_4(NO_2)_2$.

[p] The structures of several 3,5-dinitrobenzoate esters were investigated—derivatives of bicyclo-octane[46], calciferol[98,99], and toxisterol[100,101].

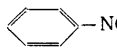
[q] The structure of 1,3-dichloro-2,4,6-trinitrobenzene is given in a handbook[67].

[r] I—centrosymmetric form, II—non-centrosymmetric form.

to analyse the relation between the geometrical parameters of the CNO_2 group in aromatic nitro-compounds[113–115].

It follows from Table 7 that, with increase in the number of nitro-groups in aromatic nitroamines and chloronitrobenzenes, the C–NH_2 and C–Cl bond lengths decrease.

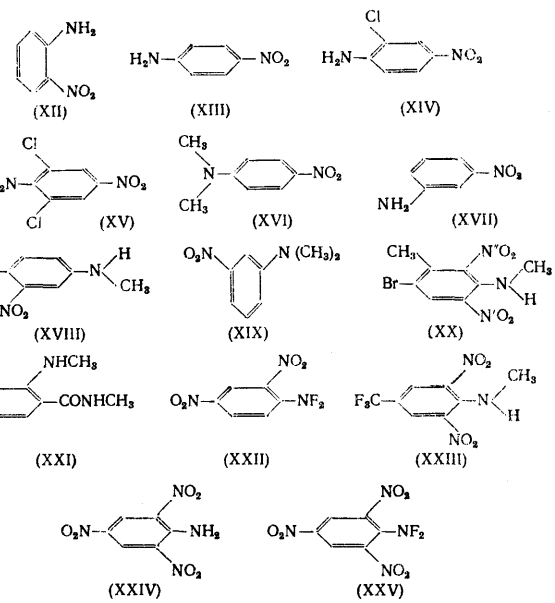
Analysis of the conformations of aromatic nitro-compounds in the crystal leads to the conclusion that the CNO_2 groups in the majority of compounds are planar or deviate insignificantly from the plane. The average CNO valence angle in the CNO_2 group is 118°, although in many cases the two angles at the same nitrogen atom have different values, apparently due to crystal field effects.

Aromatic nitro-compounds in which there are no bulky substituents next to the nitro-group have a planar or nearly planar conformation of the fragment . Such a conformation is characteristic of *meta*- and *para*-substituted nitrobenzenes[111–116] (Table 8). In the presence of bulky *ortho*-substituents next to the nitro-group the latter rotates about the C–N bonds†. The average angles of rotation of the NO_2 groups in the absence and presence of one and two *ortho*-substituents have been calculated[116], 6°, 40°, and 63° being obtained respectively.

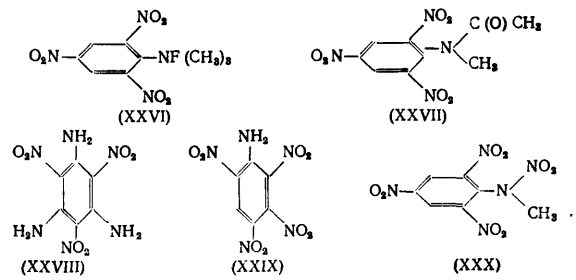
The question of the dependence of the C–NO_2 bond length on the angle of rotation of the nitro-groups has been discussed in the literature for a long time[117,118]. Such a dependence does not follow from the analysis of numerous experimental data[111]. Admittedly, the shortest C–NO_2 bonds refer to the CNO_2 groups having small angles of rotation, but the converse conclusion is not valid.

From the standpoint of the problem of the mutual influence of atoms and groups of atoms in molecules and when account is taken of the conformational characteristics, is is necessary to examine separately the structures of aromatic nitroamines, o-nitrophenols, polynuclear nitro-compounds, and also π-complexes of trinitrobenzene and its substituted derivatives.

The structural characteristics of aromatic nitroamines are associated with the mutual influence of the nitro- and amino-groups (Table 9).

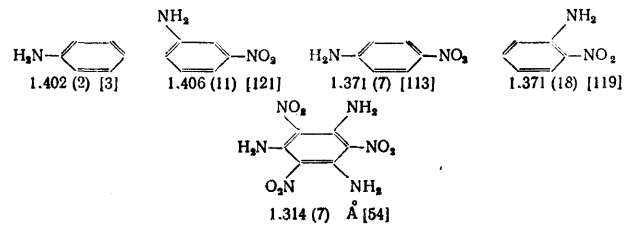


† Primary amines and phenols, in which there is a hydrogen bond, are an exception (see below).



Analysis of data for primary aromatic amines led the authors[129] to conclude that aromatic amines without the nitro-group have the longest C–NH_2 bond lengths, amines with *para*-nitro-groups have bonds of medium length, and those with *ortho*-nitro-groups have the shortest bonds.

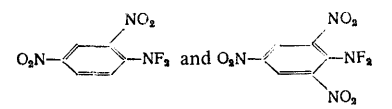
A recent X-ray diffraction study of the γ-modification of o-nitroaniline[119] showed that the C–NH_2 bond length in this compound is the same as in p-nitroaniline. An appreciable shortening of the C–N_{amine} bonds has been observed in polynitroanilines:



Note. Here and in the other formulae the numbers in square brackets denote references (Ed.of Translation).

The shortening of the C–N_{amine} bonds is a consequence of the influence of nitro-groups in the o- or p-positions relative to the amino-group.

The substitution of the hydrogen atoms in the NH_2 group by the more electronegative fluorine atoms leads to an appreciable lengthening of the C–N_{amine} bond to 1.46 Å, as shown by a study of

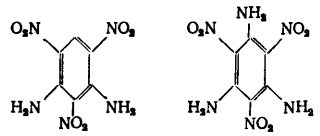


The parameters of the CNO_2 group, i.e. r(C–N), r(N=O), and ∠ONO, change less than r(C–N_{amine}), which leads to the conclusion that the effect of the interaction of the NH_2 and NO_2 groups is manifested to the greatest extent by a change in the length of the C–N_{amine} bond and is small for the CNO_2 group.

The deformations of the benzene ring caused by substituents are particularly pronounced in aromatic nitroamines[108]. The $CC_{NO_2}C$ valence angle is as a rule increased, while ∠$CC_{NH_2}C$ is reduced on average by 2–3° compared with benzene. In polynitroamines the deviations of the $CC_{NH_2}C$ angles from 120° reach 5°. In p-nitroaniline the C⋯C bonds in the benzene ring were found to be non-equivalent, with formation of the quinonoid structure , the $CC_{NO_2}C$ angle is 121.4(0.4)°, and the $CC_{NH_2}C$ angle is 118.9(0.4)°.

A planar configuration of the bonds involving the amino-nitrogen atom is characteristic of m- and p-nitroanilines and their derivatives. In the absence of other substituents, the

m- and *p*-nitroaniline molecules are on the whole planar. A planar structure has also been observed for the molecule of *p*-nitroaniline and polynitroamines containing adjoining nitro- and unsubstituted amino-groups, for example;



This is associated with the formation of hydrogen bonds of the type $NH_2 \ldots O_2N$.

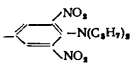
Table 9. The carbon–nitrogen bond lengths (Å) in the molecules of a series of nitro-derivatives of aromatic amines.

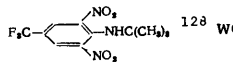
Compound	$C_{ph}-N_{nitro}$	$C_{ph}-N_{amine}$	Refs.	Compound	$C_{ph}-N_{nitro}$	$C_{ph}-N_{amine}$	Refs.
(XII)	1.490 (20)	1.371 (18)	[119]	(XXIII)	1.443 (7)	1.331 (7)	[126][d]
(XIII)	1.460 (7)	1.371 (7)	[113]	(XXIV)	1.471 (5)	1.340 (5)	[129]
(XIV)	1.471 (13)	1.386 (12)	[54]	(XXV)	1.487 (4)	1.461 (4)	[130]
(XV)	1.466 (5)	1.358 (5)	[120]	(XXVI)	1.481 (3)	1.414 (3)	[131]
(XVI)	1.405 (16)	1.358 (16)	[54][a]	(XXVII)	1.487 (3)	1.417 (2)	[132]
(XVII)	1.440 (16)	1.406 (11)	[121]	(XXVIII)	1.419 (3)	1.314 (7)	[54][e]
(XVIII)	1.474 (6)	1.377 (6)	[122][b]	(XXIX)	1.465 (6)	1.312 (6)	[68][f]
(XIX)	1.492 (1)	1.404 (9)	[123]	(XXX)	1.490 (5)	1.497 (4)	[67][g]
(XX)	CN′:1.429 (8) CN″:1.481 (8)	1.320 (8)	[67]				
(XXI)	CN′:1.456 (5) CN″:1.432 (5)	1.343 (3)	[124]				
(XXII)	1.475 (2)[c]	1.464 (2)	[125]				

[a] For structural data on 2,6-dichloro-*N*,*N*-dimethyl-4-nitroaniline, see Ref. 54.

[b] The structure of *p*-bromo-*N*-methyl-*m*-nitroaniline is also described.

[c] Here and henceforth the average values of $r(C-NO_2)$ are given.

[d] The structure of Cl– [127] and

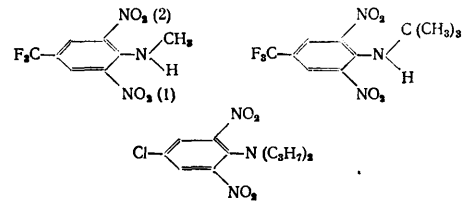
 [128] were also investigated.

[e] There exist data of low accuracy (σ_r = 0.02 Å, $\sigma_\angle$ = 2°) for the 1,3-diamino-2,4,6-trinitrobenzene[67].

[f] The geometrical parameters of the $N(NO_2)CH_3$ group are $r(N-NO_2)$ = 1.348(4) Å, $r(N-CH_3)$ = 1.466(9) Å, and $\angle NNCH_3$ = 118.8(0.3)°; the angle of rotation of this group about the $C_{ph}-N$ bond is 65°.

[g] There are also data for β,β,β-trifluoroethyl-2,4,6-tetranitroaniline[44].

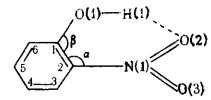
The substitution of hydrogen atoms in the amino-group by more bulky groups infringes the planarity of the molecules, as has been shown in a series of studies[126–128] of aliphatic *N*-substituted derivatives of 2,6-dinitroanilines:



The crystals of $CF_3C_6H_2(NO_2)_2NHCH_3$ contain two types of molecules whose conformations are identical: the nitro-group (1) is almost coplanar with the ring, while the nitro-group (2), closest to the methyl group, has been rotated by approximately 50°. A similar conformation has been observed in $CF_3C_6H_2(NO_2)_2NHC(CH_3)_3$. Both nitro-groups in $ClC_6H_2 \cdot (NO_2)_2N(C_3H_7)_2$ have been rotated by approximately 52° out of plane of the ring and their planes form an angle of 83° relative to one another.

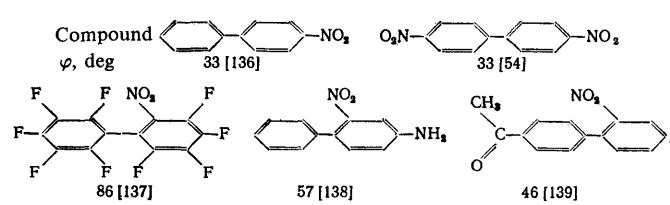
The planar configuration of the bonds involving the nitrogen atom changes to a significantly pyramidal configuration when a hydrogen atom in the NH_2 group is replaced by fluorine, i.e. in the compounds $(NO_2)_2C_6H_3NF_2$ and $(NO_2)_3 \cdot C_6H_2NF_2$. In the molecules of these compounds the nitro-groups have been appreciably rotated relative to the plane of the benzene ring.

A characteristic feature of the structure of *o*-nitrophenols (Table 8) is the formation of an intramolecular hydrogen bond between the OH and NO_2 groups. The geometry of these groups of bonds



is characterised by the following features[133]: (1) short O(1)...O(2) (2.55–2.60 Å) and H...O(2) contacts; (2) small (∠14°) angles of twist τ for rotation about the O(1)–C(1) and C–N bonds; (3) large NCC(α) and CCO(β) angles. As a rule, the N=O bonds of the nitro-group adjoining the OH group are also found to be non-equivalent: the N(1)=O(3) bond is shorter than the N(1)=O(2) bond involved in the formation of a hydrogen bond. A detailed analysis of the bond lengths in *o*-nitrophenols and nitrophenoxides has been carried out[134].

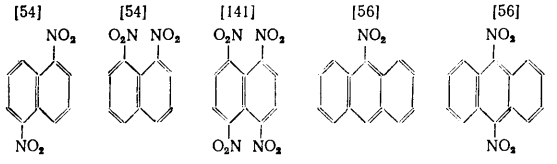
Polynuclear aromatic nitro-compounds—derivatives of biphenyl and condensed aromatic hydrocarbons—have a number of conformational characteristics. According to numerous structural data, the most significant conformational distortion of the molecules of biphenyl and its derivatives consists in the rotation (by an angle φ) of one benzene ring relative to the other about the $C_{benz}-C_{benz}$ bond[135]. The following data are available for crystalline nitrobiphenyl derivatives:



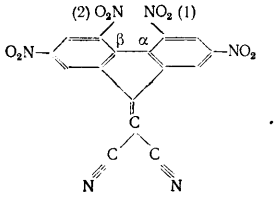
These show that the maximum angle of rotation of the ring

ϕ_{C-C} is observed in 2-nitrononafluorobiphenyl[137]#. The angle of rotation of the nitro-group in the same compound is also large (56°). A virtually coplanar disposition of the nitro-groups and the benzene ring has been noted in compounds with *p*-nitro-groups, i.e. the conformation is the same as for *p*-substituted benzene derivatives. For example, the angle of rotation of the NO_2 group in 4-nitrobiphenyl is 2°, while those in 4,4'-dinitrobiphenyl are 0° and 11°. The length of the $C_{benz}\cdots C_{benz}$ central bond in nitrobiphenyl derivatives is the same as in biphenyl (1.49 Å).

The steric hindrance in the molecules of nitro-compounds with condensed benzene rings



leads to larger angles of rotation of the nitro-groups relative to the plane of the ring and to deformations of the outer valence angles[135]. For example, the nitro-groups in 1,5-dinitronaphthalene have been rotated by 49°, those in 9,10-dinitroanthracene have been rotated by 64°, etc. The steric hindrance in 1,8-dinitronaphthalene causes the rotation of the nitro-groups by 43° relative to the plane of the ring, the displacement of the nitrogen atoms from this plane by 0.4 Å, and the deformation of the NCC valence angles by approximately 3°. The proximity of nitro-groups (1) and (2) in the 9-dicyanomethylene-2,4,5,7-tetranitrofluorene molecule[142] leads to the rotation of these groups by 35° and to an increase of the angles α and β to 123° and 134° respectively:



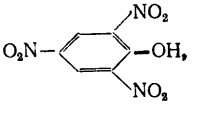
Thus in the analysis of the molecular structure of polynuclear nitro-compounds it is necessary to take into account steric factors, which frequently play a decisive role in the geometry of compounds of this class.

Unsubstituted and substituted polynitro-compounds form a series of complexes with aromatic hydrocarbons, quinhydrone, and aromatic iodo-hydrocarbons[143]. The crystal chemistry of molecular donor–acceptor π-complexes, including those of *sym*-trinitrobenzene, has been reviewed[144]. According to X-ray diffraction data, complex formation does not alter or hardly alters the molecular geometry of the donor and acceptor. In all the π-complexes of *sym*-trinitrobenzene its benzene ring is planar within the limits of experimental error, but in certain complexes, for example in the complex with acepleiadylene[68], there are slight deviations of two carbon atoms from the average plane of the benzene ring. The nitrogen atoms are also virtually in the plane of the ring. The nitro-groups are as a rule rotated by small angles (on average by 4°, at most by 18°), the angles being determined by steric effects, the packing requirements, the interaction of the donor and acceptor, etc.

The principal geometrical parameters of *sym*-trinitrobenzene in the complexes, such as $r(C-N)$, $r(C\cdots C)$, ∠ONO, and ∠CCC (according to the most accurate experimental data)[54], do not vary as a function of the donor. The significant scatter of the values of $r(N=O)$ may be associated with the appreciable thermal vibrations of the nitro-group.

For the complexes of substituted trinitrobenzene derivatives, the above factors influencing the rotation of the nitro-group relative to the plane of the benzene ring are supplemented by the influence of the substituent and, as a rule, the angle of rotation of the nitro-groups in the *o*-positions relative to the substituent is much greater than for the nitro-groups in the *p*-positions.

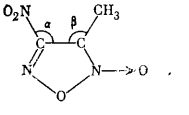
The characteristics of the structure of picric acid



which are analogous to those observed for *o*-nitrophenols and are due to the formation of an intramolecular hydrogen bond, persist in its π-complexes. The donors in these complexes are anthracene[145], pyridine[146], and 2-amino-1-bromonaphthalene[61].

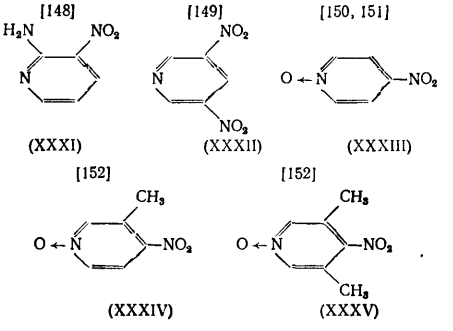
3. Heterocyclic and Organoelemental Nitro-Compounds

The heterocyclic nitro-compounds investigated are fairly varied. The nitro-group in 3-methyl-4-nitrofuroxan[147] is linked directly to the five-membered ring:



The close proximity of the NO_2 and CH_3 groups leads to conformational distortions: α = 125.7°, β = 135.3°, and ϕ_{NO_2} = 17°. The heterocyclic ring is planar with distorted valence angles. The parameters of the CNO_2 group are the same as in aromatic nitro-compounds.

The structures of derivatives of nitropyridine have been studied in greatest detail:

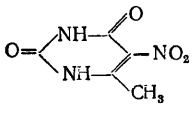


In the 2-amino-3-nitropyridine (XXXI) molecule, where the nitro-group adjoins the amino-group, one may note a decrease of $r(C-NH_2)$ to 1.336 Å, similar to that observed for aromatic

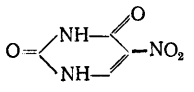
In 6,6'-dinitrophenyl-2,2'-dicarboxylic acid, which has been recently investigated[140], the angle of rotation of the rings is 71° and the angle of rotation of the *o*-nitro-groups is 30°.

nitroamines, and a slight shortening of the C–NO_2 bond to 1.440 Å. The $C_{NH_2}\cdots C_{NO_2}$ bond in the pyridine ring (1.412 Å) is somewhat longer than the other bonds in the ring (1.33–1.39 Å), while the amino-group is planar. There is an intramolecular NH...ON hydrogen bond and in the crystal the molecules are linked by NH...N_{ring} hydrogen bonds.

The molecules of 3,5-dinitropyridine (XXXII) and 4-nitropyridine *N*-oxide (XXXIII) are planar. In contrast to compound (XXXIII), the molecules of derivatives of 4-nitropyridine oxide (XXXIV) and (XXXV) are non-planar. In compound (XXXIV) the rotation of the nitro-group adjoining the CH_3 group is slight (approximately 17°). In compound (XXXV) two methyl groups are in the *ortho*-positions relative to the NO_2 group, and the angle ϕ_{NO_2} has increased to approximately 50°. It is of interest that the introduction of only one methyl group next to the nitro-group in 6-methyl-5-nitrouracil[153]



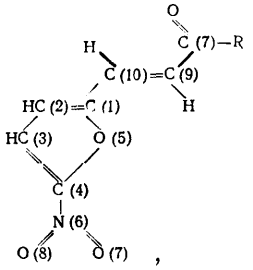
leads to the rotation of the latter by approximately 40°. The molecule of 5-nitrouracil[67]



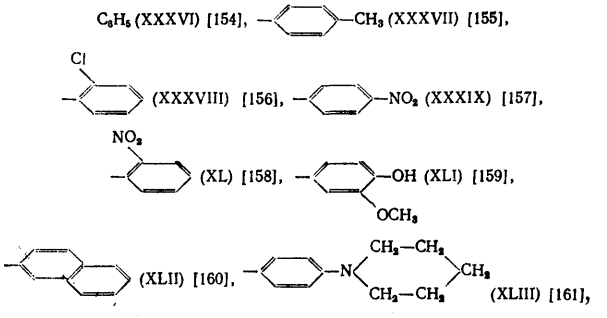
is planar.

Thus the influence of the heterocycle in the heterocyclic nitro-compounds examined hardly affects the parameters of the CNO_2 group: they are the same as for aromatic nitro-compounds.

The structure of nitrofuranylpropenes having the general formula

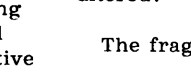


where R is

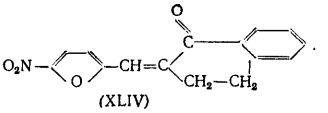


has been studied in a series of investigations[154–161].

The $C-NO_2$ bond in the CNO_2 group linked to the furan ring is shorter (1.42 Å) than in aromatic nitro-compounds on average by 0.05 Å. A slight non-equivalence of the CNO angles has been noted, but it does exceed the experimental error, the angle C(4)N(6)O(7) being greater than the angle C(4)N(6)O(8) by 2–3°. The outer angles which the nitro-group makes with the furan ring, namely ∠C(3)C(4)N(6) and ∠O(5)C(4)N(6), are respectively 130° and 117°. On the whole, the parameters of the furan ring in the compounds considered differ only slightly from those found for the furan molecule in the gas phase[3], but the ring symmetry C_2 is altered.

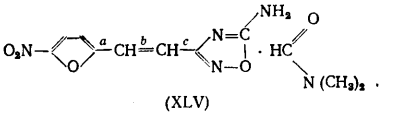
The fragment  has a cisoid configuration in the majority of compounds. The molecules of compounds (XXXVI), (XXXVII), (XXXIX), and (XLII) are planar. The non-planarity of the molecules of compounds (XXXVIII), (XL), (XLI), and (XLIII) arises only as regards the substituent R.

The series of studies examined above includes also an investigation of the molecule of compound (XLIV):[162]



(XLIV)

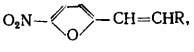
and of the complex (XLV)[163]



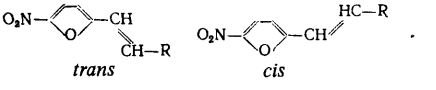
(XLV)

The parameters of the nitrofuran fragment in compounds (XLIV) and (XLV) are analogous to those discussed above. The bonds *a*, *b*, and *c* in the planar molecule of *trans*-5-amino-3-[2-(4-nitro-2-furyl)vinyl]-1,2,4-oxadiazole in complex (XLV) have the *trans*-configuration.

The structure of derivatives of 5-nitro-2-vinylfuran

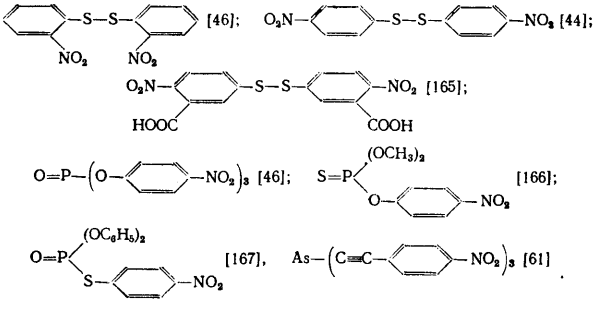


where R = $SO_2C_6H_4Cl$, $SO_2C_6H_4CH_3$, or $N(CH_3)_2$, has been investigated[164]. It has been noted that the conformation of these compounds depends on the nature of the substituent R: the *trans*-structure is preferred for compounds with electron-accepting substituents and the *cis*-structure is preferred for those with electron-donating substituents.



trans *cis*

The available structural data for organoelemental nitro-compounds are limited. The following nitro-derivatives of sulphur, phosphorus, and arsenic compounds have been studied:



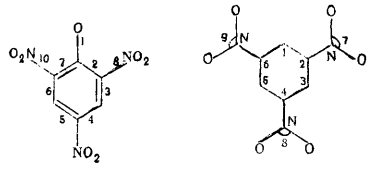
No significant deviations from the general rules governing the structure of aromatic nitro-compounds have been observed in the aromatic nitro-component.

4. Anions of Aromatic Nitro-Compounds

Changes in the geometrical parameters of the aromatic nitro-fragment have been observed in aromatic nitro-anions compared with the neutral molecules. Thus the N=O bond lengths are greater and the ONO angles are reduced to less than 120° in a series of anions. The shortening of the $C-NO_2$ bond by 0.05–0.07 Å has been noted in picrates, phenoxides, Meisenheimer salts, and certain other anions. It is believed[168] that the decrease of the length of this bond depends on the stronger interaction between the NO_2 group and the ring. The $CC_{NO_2}C$ angles in the aromatic rings of 4-hydroxy-5,7-dinitrofurazan anions[168] and in the corresponding Meisenheimer salt involving one of the nitro-groups are not increased, as is usually the case, but are actually reduced to 118.5°, which is probably associated with the influence of the furazan ring[169]. In these compounds both nitro-groups are virtually coplanar with the ring, despite the presence of the *ortho*-substituent.

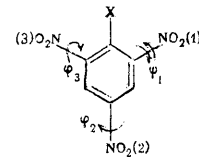
The bond lengths and valence angles in nitrophenoxides and picrates have been analysed[134] and a significant alteration of the geometry of the benzene ring in the anion has been demonstrated: bonds 2 and 7 of the C···C type have been lengthened to 1.45 Å, the CCC angle between these bonds has been reduced to 112°, and the bond lengths $r(C-O)$ and $r(C-NO_2)$ have also been altered (Table 10).

Table 10. The weighted-mean values of the parameters of nitrophenoxides and picrates (averaged with respect to 12 molecules).



Type of bond	r, Å	Type of angle	Angle, deg	Type of bond	r, Å	Type of angle	Angle, deg
1	1.248	1	111.8	6	1.370	6	124.1
2	1.451	2	123.8	7	1.444	7	121.6
3	1.373	3	119.6	8	1.452	8	122.6
4	1.380	4	121.2	9	1.445	9	120.7
5	1.384	5	119.3	10	1.443		

An interesting conformational feature has been noted on comparing the angles of rotation of the nitro-groups in picryl halides and their complexes as well as picrates[170]. It was found that in some of the compounds indicated, particularly in potassium and ammonium picrates, the nitro-groups (1) and (3) rotate in the same direction and the molecules have the C_2 symmetry with $\phi_1 = \phi_3$. In other compounds, for example, in complexes of picryl bromide with fluoranthene and pyrene, the nitro-groups (1) and (3) rotate in opposite directions and the molecular symmetry is C_S.



Comparison of the anions of aliphatic and aromatic nitro-compounds shows that the geometry of the anions of aliphatic nitro-compounds is on the whole altered less relative to neutral molecules.

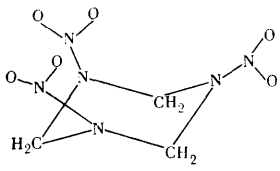
Table 11. The bond lengths (Å) and the valence angles (deg) in the nitroamino-groups in the molecules of cyclic nitro-amines*.

Molecule	r(N=O)	r(N–N)	r(N–C)	∠ONO	∠CNC
Hexogen (XLVI) (Ref.171)	1.201 (5); 1.205 (5)	1.398 (3)	1.440 (4); 1.458 (4)	125.5 (0.4)	114.8 (0.2)
	1.203 (5) 1.207 (5)	1.392 (3)	1.443 (4); 1.468 (4)	125.7 (0.4)	114.6 (0.2)
	1.209 (5); 1.233 (4)	1.351 (3)	1.450 (4); 1.464 (4)	125.0 (0.3)	115.1 (0.2)
α-Octogen (XLVIIa) (Ref.54)	1.215 (13); 1.238 (13)	1.354 (10)	1.445 (13); 1.450 (14)	125 (2)	124 (1)
	1.225 (10); 1.235 (10)	1.367 (12)	1.447 (13); 1.470 (14)	125 (2)	120 (4)
β-Octogen (XLVIIb) (Ref.56)	1.222 (8); 1.233 (8)	1.354 (5)	1.448 (7); 1.471 (6)	125.9 (0.6)	122.4 (0.4)
	1.204 (8); 1.210 (8)	1.373 (5)	1.437 (6); 1.455 (6)	126.7 (0.5)	123.8 (0.4)
δ-Octogen (Ref.172)	1.210 (25); 1.250 (15)	1.355 (23)	1.470 (23); 1.485 (19)	126.0 (1.8)	121.5 (1.4)
	1.240 (12); 1.187 (23)	1.363 (20)	1.472 (12); 1.461 (21)	121.3 (1.7)	116.6 (1.5)
	1.245 (23) 1.212 (23)	1.346 (25)	1.445 (24); 1.473 (12)	122.7 (1.9)	119.3 (1.5)
	1.201 (21); 1.113 (21)	1.392 (12)	1.500 (20); 1.442 (25)	126.3 (1.0)	119.6 (0.8)
Octogen in complex with DMF (Ref.173)	1.225 (4); 1.222 (3)	1.363 (4)	1.450 (4); 1.458 (3)	125.2 (0.3)	123.8 (0.2)
	1.220 (4); 1.217 (4)	1.377 (4)	1.459 (4); 1.453 (4)		119.7 (0.3)
(XLVIII) (Ref.174)	1.221 (2); 1.232 (2)	1.352 (2)	1.481 (2); 1.461 (2)	124.4 (0.1)	122.4 (0.1)
(XLIX) (Ref.175)	1.232 (2); 1.235 (2)	1.347 (2)	1.485 (2); 1.493 (2)	123.9 (0.2)	118.2 (0.1)
	1.225 (2); 1.223 (2)	1.386 (2)	1.485 (2); 1.490 (2)	124.3 (0.2)	113.2 (0.2)
Average values	1.221	1.367	1.463	124.9	119.3

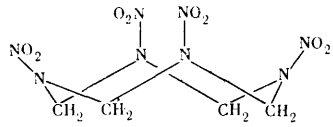
*Each row in the Table corresponds to one of the $CNNO_2$ groups.

5. *N*-Nitro- and *O*-Nitro-Compounds

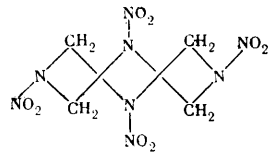
A series of *N*-nitro- and *O*-nitro-compounds, among which cyclic nitroamines occupy the principal place (Table 11), have been studied in the crystalline state.



(XLVI)



(XLVIIa)



(XLVIIб)

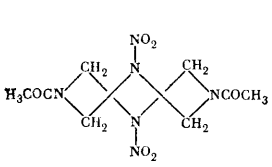
The six-membered ring of the molecule of hexogen (XLVI) has the chair conformation with two N–N bonds (1.41 Å) almost parallel with one another and approximately perpendicular to the average plane of the ring atoms; the third N–N bond (1.35 Å) is located in this plane. The molecular symmetry is C_1. The angle by which the N–N bonds are displaced from the C–N–C plane are 21.5°, 33.0°, and 32.4°. We may note that in solution the hexogen molecule has the C_3 symmetry ($\gamma = 0°$).[176]

Four crystalline modifications (α, β, γ, and δ) of octogen (XLVII) are known. The structures of α-, β-, and γ-octogens have now been determined. The crown conformation has now been established for the molecule of α-octogen (XLVIIa). Two nitroamino-groups have the equatorial conformation, while two others have the axial conformation. The planes of the neighbouring nitroamino-groups are almost perpendicular to one another. The dihedral CNNO angles are 4° and 10°.

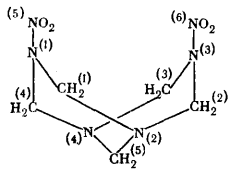
The crystal structure of β-octogen (XLVIIb) was first investigated by X-ray diffraction in 1955 [56] and was revised in 1963.[54] In 1970 the crystal structure of β-octogen was investigated by neutron diffraction[46] and it was established that the eight-membered ring of this compound has the twisted chair configuration. The $CNNO_2$ fragments of the molecule are almost planar (the dihedral CNNO angles are 0° and 10°). The angles by which the N–N bonds are displaced from the CNC planes are 4° and 17°. The two neighbouring nitroamino-groups are located in mutually perpendicular planes. In the methylene groups the HCH plane is perpendicular to the NCN plane. All the hydrogen atoms are close to the neighbouring oxygen atoms and some of them form intramolecular and intermolecular hydrogen bonds of the type CH...O.

The δ-octogen molecule resembles that of α-octogen. The C_2N-NO_2 groups are almost planar; the four carbon atoms of the ring lie in the same plane; the axis perpendicular to this plane is a twofold axis (we may note that the α-octogen molecule has a C_2 crystallographic symmetry). The study of the complex of octogen with dimethylformamide (DMF) [174] showed that its octogen molecule has a C_2 crystallographic symmetry and is similar in form to the molecules of the α- and δ-modifications. It is characterised by parameters which are comparable to those found for α-, β-, and δ-octogens. The nitroamino-groups are almost planar.

The structure of 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetra-azacyclo-octane (XLVIII) has been determined[175].



(XLVIII)



(XLIX)

As for β-octogen, the same C_1 molecular symmetry and twisted chair conformation have been established. The C and O atoms of the $COCH_3$ group and the NO_2 group are located in the same plane with the nitrogen atoms to which they are attached. The bond lengths and valence angles in the molecule of compound (XLIII) are close to those found for α-, β-, and δ-octogens.

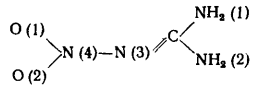
The cyclic nitroamine 3,7-dinitro-1,3,5,7-tetra-azabicyclo-[3,3,1]nonane (XLIX) [176] is an intermediate in the synthesis of octogen and hexogen. The molecule of this compound contains the eight-membered C,N-ring of octogen and the six-membered C,N-ring of hexogen. The two NNO_2 groups are planar. The dihedral angles between the NNO_2 and CNN planes are 26° and 34°. The molecule has an approximate plane of symmetry passing through the N(5), N(1), C(5), N(3), and N(6) atoms. The molecule is structurally more similar to hexogen than to octogen. Table 11 shows that the C–N bonds in the nitroamino-groups of compound (XLIX) are longer by 0.02–0.05 Å than in octogen and hexogen. The CNC angles, which are on average 115.6°, are much smaller than the corresponding angles in octogen, but agree with the angles in hexogen.

There are a number of structural data for open-chain nitroamines: NH_2NO_2;[56] $(CH_3)_2NNO_2$,[56] and $O_2NNHCH_2CH_2.NHNO_2$.[61] The structures of nitroamine and dimethylnitroamine have been investigated with a low accuracy. The NH_2NO_2 molecule is planar in the crystal, in contrast to the gas phase. In the crystalline state dimethylnitroamine has the same planar molecular configuration as in the gas phase, but the N–N bond length is greatly reduced [1.25(5) Å]. $CNHNO_2$ groups in the *N,N'*-dinitroethylenediamine molecule are planar, but the molecule as a whole is non-planar with a dihedral angle of 84° between the CCN and CNN planes. The N–N bond length is 1.301(4) Å.

A planar configuration of the amino–nitrogen bonds is characteristic of two *N*-substituted derivatives of tetranitroaniline (Table 9). The N–N bond length in *N*-methyl-*N*,2,4,6-tetranitroaniline (tetryl)[67] is 1.35 Å and the $N\begin{smallmatrix}NO_2\\CH_3\end{smallmatrix}$ group has been rotated relative to the plane of the benzene ring by 65°. The N–N bond in *N*,*N*-(β,β,β-trifluoroethyl)-*N*,2,4,6-tetranitroaniline[44] is longer than in tetryl (1.41 Å) and the angle of rotation of the group $-N\begin{smallmatrix}NO_2\\CH_2CF_2\end{smallmatrix}$ relative to the plane of the ring is 86°.

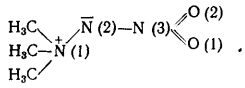
The planarity of the $-C\begin{smallmatrix}\diagup\\\diagdown\end{smallmatrix}N-NO_2\begin{smallmatrix}\diagdown\\\diagup\end{smallmatrix}C-$ group with $r(N-N)$ = 1.357(5) Å in 2,2'-dinitratoethylenenitroamine $O_2NN(CH_2CH_2.ONO_2)_2$ [177] has been established by X-ray diffraction. Other parameters of this molecule are discussed below.

The structures of a number of *N*-nitro-compounds which do not belong to the class of nitro-amines have also been studied. The nitroguanidine molecule[56]



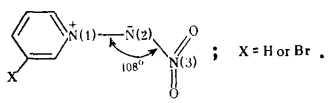
is planar with an N–N bond length of 1.35(1) Å. The steric hindrance arising between the N(1) and O(1) atoms increases the O(1)N(4)N(3) and N(1)CN(3) valence angles to 124° and 129° respectively. The remaining angles do not deviate from the usual values.

The structure of trimethylammonium nitroamidate, which is an ylid, has been investigated[178]. The N(1)–N(2) bond length [1.47(1) Å] in this molecule is close to that found in hydrazine (1.45 Å), i.e. it is a single bond.

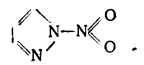


On the other hand, the bond lengths in the N–NO_2 fragment have unusual values: r(N–NO_2) = 1.32(1) Å [longer than the N=N double bond (1.25 Å) but shorter than the N–N bonds in nitroamines]; the N=O bond length [1.26(1) Å] exceeds somewhat the values usual for the NO_2 group. The authors[178] believe that this occurs owing to the considerable delocalisation in the charge in the nitro-group. The N(1)N(2)N(3)O(1) dihedral angle is approximately 0°.

In 1974 a large group of investigators published structural data for two representatives of heterocyclic *N*-nitroimides–pyridine 1-nitroimide and its bromo-derivative[179].



In these compounds the $\overset{+}{N}-\overset{-}{N}-NO_2$ system is almost planar and the dihedral angle relative to the plane of the ring is 72° for unsubstituted pyridine 1-nitroimide and 78° for its bromo-derivative. The bond lengths r(Å) are 1.42, 1.34, and 1.25 for N(1)–N(2), N(2)–N(3), and N=O respectively. Compared with the $(CH_3)_3\overset{+}{N}-\overset{-}{N}-NO_2$ system, the N(1)–N(2) bond is considerably shorter, the N(3)–N(4) bond is lengthened, and the NNN angle is reduced. We may note that the N(2)–N(3) bond length in this compound is close to r(N–N) in cyclic nitroamines. *N*-Nitropyrazole[180] also belongs to the class of compounds containing the N–NO_2 bond.

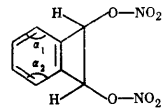


The molecule is planar and the N–NO_2 bond length (1.399 Å) and the ONO angle (128.5°) are somewhat increased relative to the average values of these parameters in crystalline nitroamines. The N–C (1.364 Å), N=C (1.315 Å), C=C (1.341 Å), and C–C (1.407 Å) bond lengths in the pyrazole ring differ from the corresponding bond lengths in unsubstituted pyrazole[3] by 0.01–0.03 Å.

Few X-ray diffraction data are available for *O*-nitro-compounds. The compound $O_2NN(CH_2CH_2ONO_2)_2$, which has been investigated[177], contains both the N–NO_2 and O–NO_2 groups with bond lengths of 1.357(5) and 1.399(6) Å respectively. The O=N=O angle in the nitroxy group (approximately 130°) is much greater than in the nitroamino-group (125°). The atoms of the molecule are located in three planes: one plane contains the atoms of the nitroamino-group $O_2N-N\begin{matrix}C\\C\end{matrix}$ and the other two planes contain the atoms of the $CONO_2$ groups.

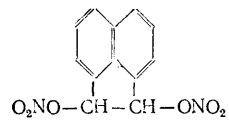
Two crystalline modifications of pentaerythritol tetranitrate $C(CH_2ONO_2)_4$ have been investigated—the low-temperature[54] and high-temperature[181] modifications. The geometrical parameters of the $CONO_2$ groups in both forms are close to the corresponding parameters of the CH_3ONO_2 molecule.

X-Ray diffraction analysis confirmed that the high-boiling isomer of benzocyclobutene 1,2-dinitrate[146] has the *cis*-configuration:



An interesting feature of the structure of this compound is the reduction of two angles in the benzene ring (α_1 and α_2) to 115°. Similar deformations of the angles have also been noted for other benzocyclobutene compounds. The bond common to the two rings (1.363 Å) has been shortened by approximately 0.02 Å relative to the average $(C\cdots C)_{benz}$ bond length, which is 1.383 Å. The length of the C(1)–C(2) bond in the cyclobutene ring is 1.561(5) Å. The nitrate groups are planar and have been rotated relative to the plane of the ring by 53° and 71°.

The dinitrate of *cis*-acenaphthene-1,2-diol



has a similar structure. The planar nitroxy-groups in this compound are inclined to the plane of the carbocyclic ring at angles of 62° and 72°.

In conclusion of this section we should note that in the cyclic nitroamines investigated the configuration of the bonds involving the nitrogen atom is planar or nearly planar. The average parameters are presented below (r in Å; the angles are expressed in degrees):

r(N=O)	r(N–N)	r(N–C)	∠CNO	∠CNC
1.221	1.367	1.463	124.9	119.3

In nitric acid esters the nitrate groups C–O(1)–N$\begin{matrix}O(2)\\O(3)\end{matrix}$ are as a rule planar with the following parameters:

r(N=O)	r(N–O(1))	r(C–O)	∠O(2)NO(3)	∠O(1)NO(2)	∠O(1)NO(3)
1.20	1.40	1.45	130	117	112

The differences between the O(1)N=O angles, which are outside the limit of the experimental error, have been explained by the steric repulsion of the C and O(2) atoms.

IV. CONCLUSION

Inspection of the combined data on nitro-compounds shows that there are distinct differences in the geometries of the NO_2 group in molecules of compounds of different classes. The N=O bond lengths vary in the range 1.20–1.24 Å with an average of 1.22 Å and the ONO valence angles vary in the range 123–133° with an average of approximately 128°. The minimum ONO angles are observed in molecules of aromatic nitro-compounds and nitroamines, while the maximum values are observed in molecules of aliphatic and alicyclic nitro-compounds. This is apparently associated with the fact that in aromatic nitro-compounds and nitroamines carbon atoms or amino-nitrogen atoms with a planar bond system are linked to the NO_2 group. The tendency towards an overall planar configuration of the NO_2 group and the groups linked to it in these molecules gives rise to a steric strain, which leads to a decrease in the ONO angle.

Analysis of structural data on aliphatic and aromatic nitro-compounds leads to the conclusion that the C–N bond lengths in the molecules of aliphatic compounds (average

1.51 Å) are greater by 0.03–0.04 Å than in the molecules of the aromatic compounds (average 1.47 Å). Similar variations are observed also in the C–C(=O)R bond lengths. The lengths of the >C–C(=O)R bonds are greater than those of >C–C(=O)R (or >C–C(=O)R) bonds by 0.03 Å.

Previously, when only a limited amount of data on the structure of nitro-compounds was available, it was noted that the lengths of different types of >C–NO_2 and >C–NO_2 bonds are equal[36]. Nowadays this conclusion must be regarded as erroneous.

Statistical analysis of the C–N bond lengths and ONO valence angles indicates a correlation between these quantities. With increase of the ONO valence angle, the C–N bond length as a rule also increases.

The planar conformation of nitroamines and aromatic nitro-compounds, in which there are no appreciable steric interactions, confirms the idea that the nitro-group is conjugated with the amino- and phenyl-groups. This is also confirmed by the finding that the amino-nitrogen atom has a planar bond configuration in contrast to the pyramidal bond configuration in the simplest amines. The effects due to the transmission of influences through the benzene ring to the *para*-position have also been observed in aromatic nitro-compounds. Steric interactions lead to the breakdown of the planar conformation of the >N–N(=O)=O and >C–N(=O)=O fragments. It is noteworthy that the >C–N(=O)=O bond length has not yet been found to vary with the angle of rotation about the C–N bond.

In aliphatic compounds the NO_2 group also influences the neighbouring bonds, but is nature is somewhat different. The conformations of the molecules of aliphatic nitro-compounds depend to a large extent on the type of groups attached to the carbon atom and on the number of nitro-groups. For a deeper understanding of the characteristics of the geometrical structure of the molecules of nitro-compounds, systematic studies are necessary.

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