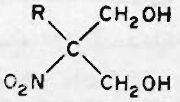
Conformational Analysis of Some Nitro & Nitroso Compounds

T. URBANSKI*
Visiting Scientist, National Chemical Laboratory, Poona 8

SINCE 1956, the author and his colleagues have been working on the problems of conformation of various acyclic and cyclic compounds containing nitro groups. Among these are C-nitro, O-nitro and N-nitro compounds. The present article gives a review of the work published so far. The work on some N-nitroso compounds is also covered.

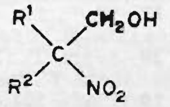
Acyclic, C-Nitro and O-Nitro Compounds

Hindered rotation in nitroalcohols — The author suggested the existence of a hydrogen bond between NO$_2$ and OH groups in nitroalcohols (I) and (II), according to structures Ia and IIa[1]. Although a certain amount of controversy has been raised[2], the suggested structures Ia and IIa seem to be generally accepted[3].



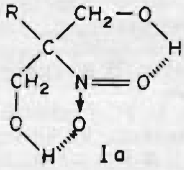
I

R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, n-C$_4$H$_9$

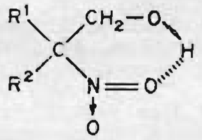


II

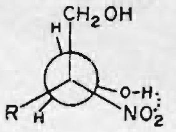
R^1 = H, R^2 = CH$_3$
R^1 = H, R^2 = C$_2$H$_5$
R^1 = R^2 = CH$_3$



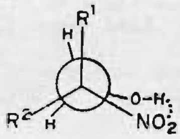
Ia



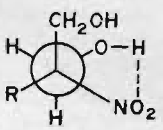
IIa



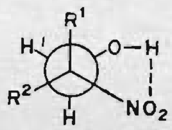
Ib



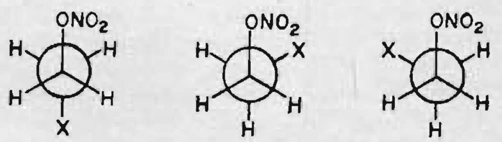
IIb



Ic



IIc



anti gauche

III

A hindered rotation in nitroalcohols (I) and (II) around the C-C bond was believed to be produced mainly by the hydrogen bond. To ascertain this, the dipole moments of the compounds (I) and (II) were calculated and also determined experimentally[4]. The values for I and II were found to be 3·35-3·50 D and 3·49-3·57 D respectively. If free rotation around the C-C bond is accepted, the μ value should be 4·1 D. For eclipsed forms Ib and IIb, the calculated μ value was 3·2 D. This should indicate that about 80% of the substances are in eclipsed forms Ib and IIb. The distance between both the oxygen atoms of the nitro groups and the oxygen atom of the hydroxylic group is of the order of 2·8 Å. Another alternative[3] is that all the molecules exist in gauche conformations Ic and IIc. The distance (as mentioned above) is here much the same — about 2·8 Å. Thus, both forms Ib-IIb and Ic-IIc are equally probable.

Hindered rotation in O-nitro compounds (*nitrate esters*) — Some O-nitro compounds show a splitting of NO$_2$ stretching vibration bands in the infrared absorption spectrum[5-7]. Rossmy[5] found that both the NO$_2$ bands — asymmetric and symmetric — were split in the spectrum of ethylene glycol dinitrate. The values for ν_{as} (NO$_2$) and ν_{sym} (NO$_2$) were 1656, 1637 cm^{-1} and 1290, 1269 cm^{-1} respectively. Rossmy suggested that the phenomenon may be due to rotational isomerism.

Urbanski and Witanowski[8] examined the spectra of 40 nitrate esters. Some of their results are given in Table 1. They came to the following conclusions: (1) splitting of both the NO$_2$ stretching vibration bands was regularly observed in the spectra of the X-CH$_2$-CH$_2$-ONO$_2$(III) type of molecules with large X substituents, such as Cl, Br, I, CN, NO$_2$ and ONO$_2$; (2) no splitting was detected when X was small, e.g. OH, or no C-C bond was present in compounds with the structure X-C-ONO$_2$, where X=CN or ONO$_2$; (3) no splitting was detected when the distance between X and ONO$_2$ was greater than in compounds III; and (4) in addition to splitting NO$_2$ bands through the hindered rotation around C-C bond, a different kind of splitting was also observed in compounds containing secondary O-nitro groups, i.e. CH-ONO$_2$. It has been established by the same workers[8] that the asymmetric stretching vibrations of nitrate esters of simple primary, secondary and tertiary alcohols can be distinguished by the frequency of the asymmetric stretching NO$_2$ vibrations: 1632-30, 1626 and 1621 cm^{-1} respectively. The frequencies are shifted to considerably higher values (1675-1640 cm^{-1}) due to the inductive effect of negative substituents.

To have confirmation for the view that splitting of NO$_2$ bands is mainly due to hindered rotation around the C-C bond, a few crystalline nitrate esters were examined in both solid and molten states. Pentaerythritol tetranitrate gave the data presented in Table 2.

Split NO$_2$ bands in crystalline pentaerythritol tetranitrate are most likely due to hindered rotation

---

*Permanent address: Polish Academy of Sciences, Warszawa, Poland and Chemical Faculty, Warsaw Institute of Technology (Politechnika), 00-662 Warszawa, Poland.

TABLE 1 — INFRARED SPECTRA OF SOME O-NITRO COMPOUNDS

Group No.*	Compound	Frequency cm^{-1} as (NO_2)	Frequency cm^{-1} sym (NO_2)
1	CH_2Cl CH_2ONO_2	1652 1640	1280
	CH_2Br CH_2ONO_2	1656 1641	1295 1282 1273
	CH_2NO_2 CH_2ONO_2	1655 1641	1284 1278
	CH_2ONO_2 CH_2ONO_2	1656	1292 1271 1235
2	CH_2OH CH_2ONO_2	1631	1282
	ONO_2 CH_2 ONO_2	1675	1283
3	CH_2ONO_2 CH_2 CH_2ONO_2	1634	1278
	CH_2ONO_2 O CH_2ONO_2	1632	1278
	CH_2ONO_2 CHOH CH_2ONO_2	1640	1283
4	CH_2ONO_2 $CHONO_2$ CH_2ONO_2	1675 1654 1645	1293 1276

*Group numbers are related to the paragraphs in text.

TABLE 2 — INFRARED SPECTRA OF PENTAERYTHRITOL

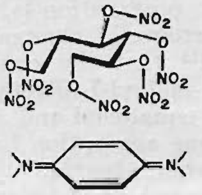
Band	Frequency, cm^{-1} Crystalline form	Frequency, cm^{-1} Melted and supercooled to 120°
(NO_2) as	1659 1647	1648
(NO_2) sym	1307 1287 1272	1276

around the C-C bonds. The hindered rotation is enhanced by the crystal lattice. Free rotation would exist in the molten state. This will include rotation around the C-C bond and the free rotation around the C-O bond postulated earlier on the basis of a relatively high dipole moment in acetone (2·5 D)[10]. It is interesting to note that the measurements of dipole moments of 1,2-dinitroethane in benzene solution suggest free rotation around C-C bond[11].

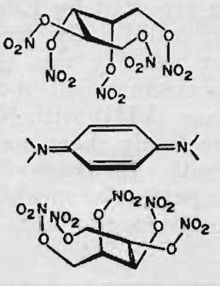
Conformation of straight chain O-nitro compounds in electron-donor-acceptor complexes — It has been found by the author and his colleagues that nitrate esters are electron acceptors and oxidize tetramethyl-*p*-phenylenediamine (TMPD) in non-polar solvents (such as 1,2-dichloroethane) to yield Wurster cation. It was further found[12,13] that esters with five to six O-nitro groups and five to six carbon atoms form EDA (charge transfer) complexes with TMPD. Unstable complexes were slowly transformed into stable complexes having the composition 1 mole TMPD-2 moles pentanitrates and 1 mole TMPD-1 mole hexanitrates. TMPD in these complexes was transformed into the tetramethyl-*p*-quinonediimine dication.

The experimental fact that all nitrate esters with one to four O-nitro groups and one to four carbon atoms do not yield EDA complexes is partly due to their relatively low enthalpy of the reaction with TMPD (and electron affinity) and partly due to more favourable structures of the complexes. It was suggested by the author that the pentanitrate of D-xylitol and the penta- and hexanitrate of D-mannitol exist in the complexes in the form of pseudo-rings. The same applies to hexanitrates of D-sorbitol and dulcitol[14].

Structure IV gives the suggested conformation of hexanitrates of chain hexitols. Structure V depicts the suggested conformation of pentanitrates of chain pentitols.



IV



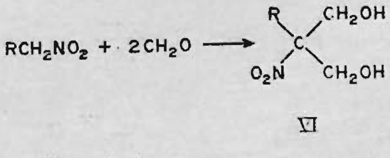
V

Heterocyclic, Non-aromatic Nitro Compounds

The heterocyclic systems discussed below were formed from primary nitroalkanes. The first step consists in adding two moles of formaldehyde to primary nitroalkanes. The aldolic addition (1) leads to the formation of diols (VI). The latter, in turn, can be converted into heterocyclic systems with the nitro group at carbon-5.

The conformation of the heterocyclic systems was studied using the following technique: (1) calculation and experimental determination of dipole moments as per the suggestion of Corey and Sneen[15] for six-member alicyclic rings. The rules of corey and Sneen were adapted to heterocyclics; (2) NMR; (3) infrared and ultraviolet absorption spectroscopy.

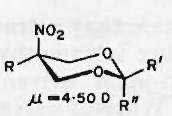
5-*Nitro*-1,3-*dioxanes* — 5-Nitro-1,3-dioxanes (VII) can be formed by reacting diols (VI) with aldehydes or ketones in anhydrous acid medium.



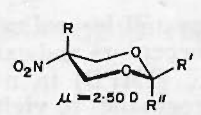
$$RCH_2NO_2 + 2CH_2O \longrightarrow \underset{O_2N\quad CH_2OH}{\overset{R\quad CH_2OH}{C}} \qquad (1)$$

VI

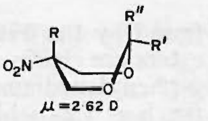
It was found that most compounds (VII) possess *trans* structure (VIIa) with an axial nitro group[16], as can be seen from the experimental and calculated



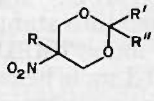
VII a



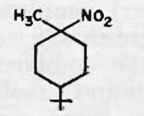
VII b



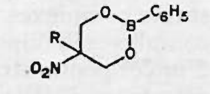
VII c



VII



VIII

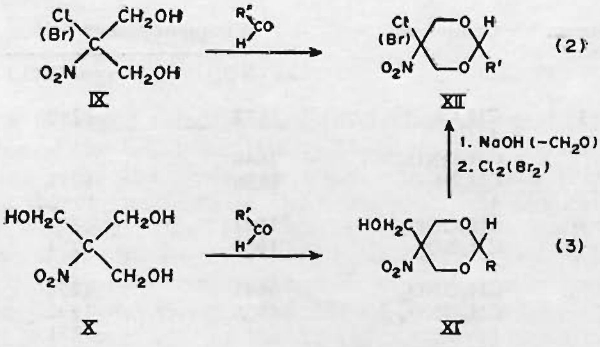


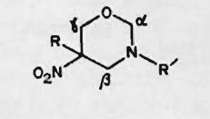
XIII

values of dipole moments (Table 3). Only compounds with R=H have the nitro group occupying the equatorial position in the *cis* form (VIIb), the boat form (VIIc) being much less probable.

It was later found that isomers VIIb along with VIIa were also formed during the ring closure reaction. However, their yield is low. The separation of isomers was achieved by gas chromatography and purification by vacuum distillation. The isolation of pure compounds VIIa and VIIb made possible their use as models for establishing the difference in the absorption spectra of the axial and equatorial NO_2 group. The results[17] are presented in Table 4. Similar results differentiating the UV absorption bands of axial and equatorial NO_2 have been reported by Eliel[18]. This observation is, however, valid only for the heterocyclic compounds described. It was established[19] that the *cis* and *trans* isomers of 4-*ter*-butyl-1-methyl-1-nitrocyclohexane (VIII) with NO_2 group equatorial and axial respectively show much the same absorption bands in both ultraviolet and infrared spectra.

A particular problem was posed by 5-halogeno derivatives of 5-nitro-1,3-dioxane (XII, R=Cl or Br). They could be prepared in two ways [(2) and (3)].



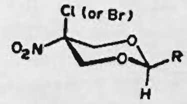


XV

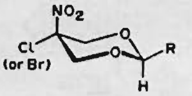
Two isomers, *cis* and *trans* XIIa and XIIb were formed in different quantities, depending on the method of their preparation. The following examples give an idea of the yields of the two isomers:

(i) Cyclization (method 2) to yield XII (R=Br) gave 94% XIIb and only 5·5% XIIa.

(ii) Bromination of XI (method 3) yielded 56-65% XIIb and 43-44% XIIa.



XII a



XII b

No appreciable difference was found in the IR frequencies of the asymmetrical vibrations of the NO_2 group in compounds XIIa and XIIb. The only characteristic feature was a wider and not sharp band of the equatorial NO_2 in XIIa.

5-*Nitro-2-bora*-1,3-*dioxanes* — By reacting diols (VI) with phenylboronic acid and its derivatives, 5-nitro-2-bora-1,3-dioxanes (XIII) were formed, substituted in position 2 by phenyl and its derivatives[16,21]. The dipole moments measured for XIII with R-CH_3, C_2H_5 and *n*-C_3H_7 were found to be in the range 4·18-4·25 D; this corresponds to a 'folded leave' shape of the ring with an axial nitro group

TABLE 3 — DIPOLE MOMENTS OF 1,3-DIOXANES (VII)

Substituents			Dipole moment	
R	R′	R″	Exp.	Calc.
CH_3, C_2H_5, *n*-C_3H_7	H	H	4·45-4·50	4·50 (VIIa)
CH_3, C_2H_5	C_6H_5	H	4·47-4·58	
CH_3, C_2H_5, *n*-C_3H_7	CH_3	CH_3	4·43-4·55	
H	H	H	2·65	2·50 (VIIb)
H	CH_3	CH_3	2·45	

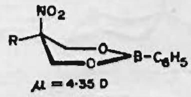
TABLE 4 — UV AND IR ABSORPTION SPECTRA OF 1,3-DIOXANES (VII)

Substituents			Absorption bands of NO_2			
R	R′	R″	Axial NO_2 (VIIa)		Equatorial NO_2 (VIIb)	
			UV nm	IR asym. cm^{-1}	UV nm	IR asym. cm^{-1}
CH_3, C_2H_5, *n*-C_3H_7	CH_3, C_2H_5, *iso*-C_3H_7, *ter*-C_4H_9	H	278-279	1556-1553 in CCl_4 1550-1548 in nujol	282-283	1548 in CCl_4 1534-1533 in nujol
CH_3, C_2H_5, *n*-C_3H_7	C_6H_5	H	278-279	1572 in $CHCl_3$ 1556-1548 in nujol	282-283	1559 in $CHCl_3$ 1536-1533 in nujol

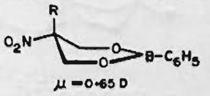
(XIIIa). The calculated value of the dipole moment is 4·35 D, whereas the isomeric form XIIIb with an axial nitro group gives a much lower value of 0·65 D.

5-*Nitro-2-sila*-1,3-*dioxanes* — By reacting dichlorodimethylsilan with diols (VI), a number of 5-nitro-2-sila-1,3-dioxanes (XIV) were prepared[16]. The observed dipole moments of the compounds with R=CH_3, C_2H_5, *N*-C_3H_7, *n*-C_4H_9 and *n*-C_5H_{11} were in the range 3·30-3·55 D. The values calculated for conformations XIVa and XIVb are 4·63 and 2·57 D respectively. This would suggest an equilibrium between two chain forms with a slight predominance of form XIVb:

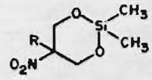
$$40\%\ \mathrm{XIVa} \rightleftharpoons 60\%\ \mathrm{XIVb} \qquad \ldots(4)$$



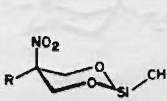
XIII a



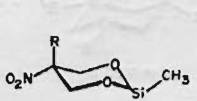
XIII b



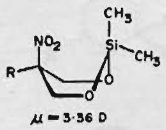
XIV



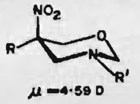
XIV a



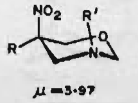
XIV b



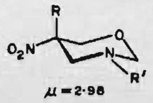
XIV c



XV a



XV b



XV c

For calculating the dipole moments, the well-known formula of the dipole moment of a mixture being equal to the square root of the sum of squares of the components was used. The values thus calculated enable the determination of the conformational enthalpy using Boltzmann distribution equation:

$$\frac{N_{\mathrm{XIVb}}}{N_{\mathrm{XIVa}}} = e^{-\Delta H/RT}$$

This gives a very low energy $-\Delta H$=0·05 kcal/mole, indicating considerable ease in changing one form to the other. Another possibility is the preferred boat conformation XVIII, which seems to be possible through the attraction between the axial NO_2 and the axial CH_3 groups.

NMR study of the system is planned. It should elucidate whether the equilibrium (4) exists.

5-*Nitrotetrahydro*-1,3-*oxazines* — 5-Nitrotetrahydro-1,3-oxazines (XV) have been prepared by the action of formaldehyde and ammonia or primary amines on diols (VI)[22].

The dipole moments of the products with (XV) R'=cyclohexyl were calculated as well as measured experimentally[23]. The experimental values were found to be 4·41-4·56 D, when R=CH_3, C_2H_5, *n*-C_3H_7, *iso*-C_3H_7 and *n*-C_4H_9 and the calculated value was 4·59 D, which showed the preferred conformation XVb. An experimental value of the same order (4·53 D) was found[16], when R' was *ter*-butyl.

However, when R' was an alkyl group, such as CH_3, C_2H_5 or *n*-C_4H_9 or an aralkyl group, such as $CH_2C_6H_5$, or *n*-C_3H_7, the dipole moments were 3·95-4·12 D, suggesting the preferred conformation XVb with the axial N-substituent, as the calculated value for this conformation was 3·97 D. The possible explanation for the axial position of the alkyls and the benzyl, with NO_2 occupying the axial position is 1,3-attracting interaction, NO_2 being the electron acceptor and alkyls or benzyl being electron donors.

It should be pointed out that the dipole moments of a number of dihydro-1,3-benzoxazines and dihydro-1,3-naphthoxazines suggest[24] a semi-chair conformation for the 1,3-oxazine ring, with a quasi-axial position of the N-substituents.

The NMR analysis of the compounds substantiated the finding of the existence of one preferred conformation with chair form[25]. The NMR spectrum contained three quartets, each corresponding to different CH_2 groups (α, β and γ) in the ring (Fig. 1).

The quartets indicate the presence of three AB two-spin systems, resulting from non-equivalence of protons within each methylene group.

If R' is *ter*-C_4H_9, which occupies an equatoria-position, similar quartets are present with only slightly different chemical shifts for β and γ methylene groups, but identical coupling constants, as can be seen in Table 5.

When R=H (XV), the measured dipole moments for R'=CH_3 and $CH_2C_6H_5$ were 3·42 and 3·36 D respectively. This should indicate an interchange

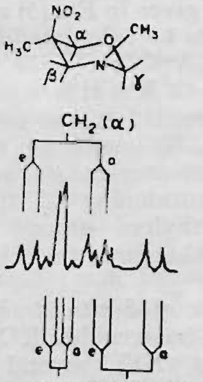
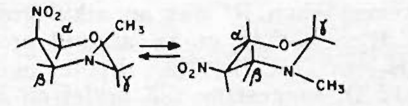


Fig. 1 — NMR spectrum of 5-nitrotetrahydro-1,3-oxazine with methyl in position 5

TABLE 5 — CHEMICAL SHIFTS AND COUPLING CONSTANTS OF XV/CONFORMATION XVb

CH^2 group	Chemical shifts /δ/ and coupling constants /J/	R and R' substituents	
		R = R' = CH_3	R = CH_3, R *ter*-C_4H_9
α	δ	0·80 ppm	0·81 ppm
	J	12 cps	12 cps
β	δ	0·70 ppm	0·84 ppm
	J	12·5 cps	12·5 cps
γ	δ	0·10 ppm	0·28 ppm
	J	9 cps	9 cps



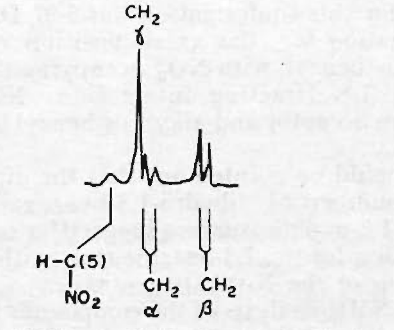


Fig. 2 — NMR spectrum of 5-nitrotetrahydro-1,3-oxazine with hydrogen in position 5

between XVb and XVc. The two forms give calculated values 3·97 D and 2·98 D respectively.

The approximate proportion of the two species is 35:65:

35% XV⇌b65% XVc …(5)

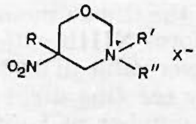
The NMR analysis confirmed this finding; the quartets collapse, and the only observable splitting into doublets results from spin-spin interaction of the α- and β-methylene groups with the hydrogen atom at C-5 (Fig. 2).

The proportion given in Eq. (5) allows the enthalpy of conformation to be calculated by Boltzmann distribution: $-\Delta H = 0{\cdot}07$ kcal/mole.

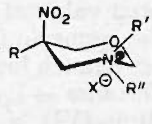
As far as XV with R′=H is concerned, no definite conclusion with regard to the conformation of the N-hydrogen (R′=H) could be drawn from both dipole moment measurements and NMR spectra. In the latter, broadening of the signals of the neighbouring methylene groups was observed as a result of the exchange of the NH protons between the molecules.

Quaternary salts of 5-*nitrotetrahydro*-1,3-*oxazine*— By adding alkyl halogenides R″X to 5-nitrotetrahydro-1,3-oxazines (XV), several quaternary salts of the general formula XVI were obtained[26]. When R″ was different from R′, two diastereoisomers were obtained (XVIa and XVIb). Assuming that the N-alkyl R′ is in the axial conformation, the incoming group R″ occupies an equatorial position. Experimental work revealed some interesting facts. According to earlier findings, R′= cyclohexyl and *ter*-butyl are in equatorial position and the compound cannot be quaternized with CH_3Br. Neither N-methyl derivative (R′=CH_3, axial) can be quaternized with *ter*-butyl bromide, most probably due to steric hinderance.

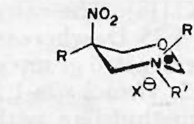
5-*Nitro*-2-*silatetrahydro*-1,3-*oxazines* — By reacting 3-amino-2-nitropropan-1-ol derivatives (XVII) [obtained from tetrahydrooxazines (XV) by ring opening] with dimethylsiladiamines, 5-nitro-2-silatetrahydro-1,3-oxazine (XVIII) derivatives were formed[27]. Compounds (XVIII) with R=C_2H_5, R′=C_2H_5 and n-C_4H_9 have shown dipole moments 4·19 D and 4·43 D respectively. The calculated values for conformations XVIIIa and XVIIIb were found to be 4·59 D and 3·22 D respectively.



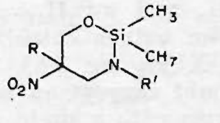
XVI



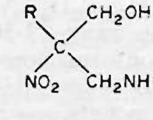
XVI a



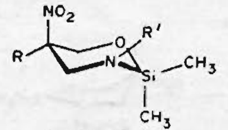
XVI b



XVIII

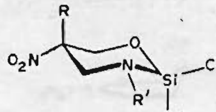


XVII



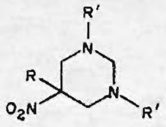
$\mu = 4{\cdot}59$ D

XVIII a

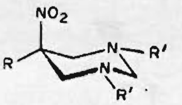


$\mu = 3{\cdot}22$ D

XVIII b

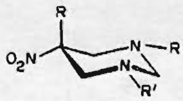


XIX



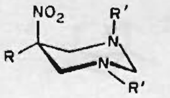
$\mu = 4{\cdot}35$ D

XIX a



$\mu = 3{\cdot}12$ D

XIX b



$\mu = 3{\cdot}72$ D

XIX c

This suggests an interchange between the two forms and the equilibrium:

80% XVIIIa ⇌ 20% XVIIIb …(6)

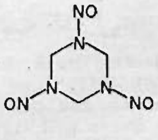
On the basis of Boltzmann distribution, the conformational energy of this conversion (—ΔH) was found to be about 0·16 kcal/mole.

5-*Nitrohexahydropyrimidines* — 5-Nitrohexahydropyrimidines (XIX) were prepared by the action of formaldehyde and two moles of primary amines on diols[28]. The dipole moments were measured and calculated for derivatives of XIX with R′= cyclohexyl and benzyl[16,29].

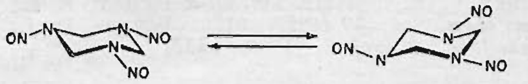
The measured dipole moments were in the range 4·36-4·45 D, when R was CH_3, C_2H_5 or n-C_3H_7; the values were in good agreement with the calculated data for conformation XIXa ($\mu = 4{\cdot}35$ D). Here, the nitro group is in the axial position and both the N-substituents are equatorial. However, when R is H, the nitro group acquires equatorial conformation and the preferred form is XIXb.

Conformation XIXa is not in agreement with the finding of Eliel and coworkers[18,30] for hexahydropyrimidines (however, without the nitro group, which exerts a strong influence on the chemical and physical properties of the ring). According to these workers, one of the N-alkyls is in axial and another in equatorial position. This was not fully substantiated by Katritzky and coworkers[31]. The difference between our finding and that of Eliel may be due to the fact that the nitro group is present in our compounds.

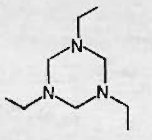
1,3,5-*Trinitro- and* 1,3,5-*trinitroso-hexahydro*-1,3,5-*triazine* — 1,3,5-Trinitrohexahydro-1,3,5-triazine, the well-known explosive (cyclonite, hexogene or RDX)[31], does not offer anything particular with regard to its conformation; it has two fast interchangeable chain forms giving only one single peak in NMR signal of CH_2 groups[32]. On the contrary, 1,3,5-trinitrosohexahydro-1,3,5-triazine (XX) offers an interesting example of ring inversion around nitrogen atoms (the anomeric effect) (Eq. 7)[32]. As a result of the lack of symmetry of the N-nitroso group, three sharp NMR signals are recorded for three methylene groups at room temperature. This can occur from the hindered rotation around the N-N bond due to the resonance structures shown in Eq. (8) and non-equivalence of the methylene groups as shown in XXα and XXβ.



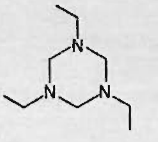
XX



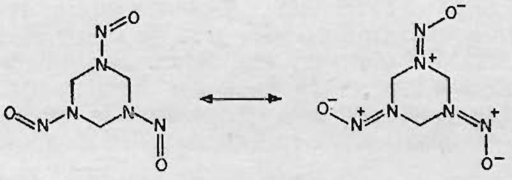
(7)



XX
α



XX
β



(8)

Three NMR signals are recorded at room temperature with intensities in the ratio 1:1·66:1. The proportion between the α and β forms is, therefore, 18:82. The theoretical calculation of statistical distribution of both forms gave the proportion 25:75. With increase in temperature above 100°, the hindered rotation is replaced by free rotation and one single peak of CH_2 group appears, narrowed gradually to a sharp signal at 208° (Fig. 3).

It was possible from the temperature dependence of the signals to calculate the activation energy of the rotation around the N-N bond. It gave the value $E_a = 22 \pm 2$ kcal/mole, which is consistent with the values for other N-nitroso compounds[34].

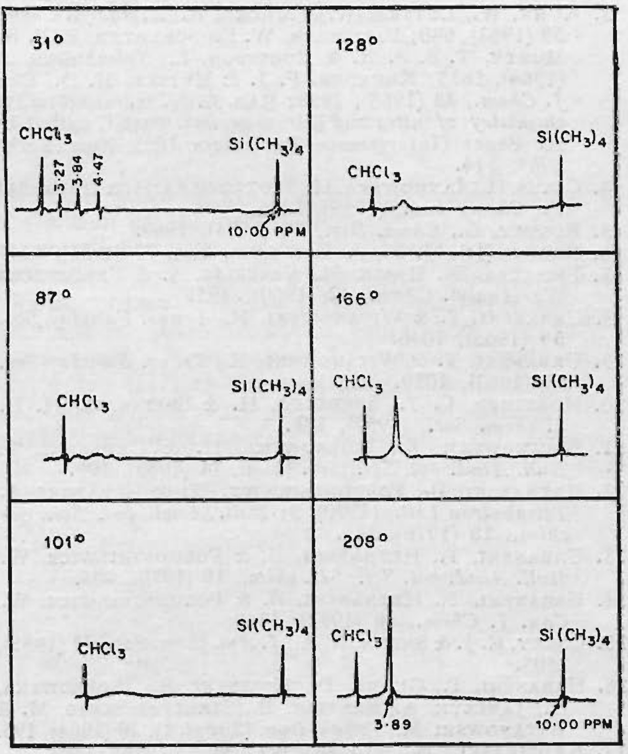


Fig. 3 — Effect of temperature change on the NMR spectrum of 1,3,5-trinitrosohexahydro-1,3,5-triazine

Summary

The work done by the author's team on conformation of compounds containing C-nitro, O-nitro, N-nitro and N-nitroso group or groups since 1956 is reviewed. The work has indicated that nitroalcohols may exist in gauche form due to the hydrogen bonding between the nitro and OH groups. O-nitro compounds show in IR spectrum a hindered rotation around C-C bond, and long chain nitrate esters (5-6 C atoms and 5-6 O-nitro groups) in some cases (under the action of strong electron donors) can be coiled into pseudo rings. The heterocyclic systems 5-nitro-1,3-dioxanes, 5-nitro-2-sila-1,3-dioxanes, 5-nitrotetrahydro-1,3-oxazines, 5-nitro-2-sila-1,3-oxazines and 5-nitrohexahydropyrimidines show the preferred conformation in chair form with the nitro group in the axial position. 5-Nitro-2-bora-1,3-dioxanes possess a "folded leave" conformation with the nitro group in the axial position. 1,3,5-Trinitrosohexahydro-1,3,5-triazine shows the aromatic effect around ring nitrogen atoms and a hindered rotation around the N-N bond.

Acknowledgement

The author's thanks are due to all his colleagues who contributed to the work described in the paper. Their names are recorded in the list of references.

References

1. Urbanski, T., *Bull. Acad. pol. Sci., Cl. III*, **1** (1953), 239; **2** (1954), 393; *Roczn. Chem.*, **29** (1955), 375; *IUPAC symposium on hydrogen bond*, Ljubljana, edited D. Hadzi (Pergamon Press Inc., New York), 1959, 143; *Tetrahedron*, **6** (1959), 1; Urbanski, T. & Ciecierska, D., *Roczn. Chem.*, **29** (1955), 11.
2. Ungnade, H. E. & Kissinger, L. W., *Tetrahedron, Suppl.* 1, **19** (1963), 121.

3. Kuhn, W., Lüttke, W. & Mecke, R., *Z. analyt. Chem.*, **59** (1963), 680; Baitinger, W. F., Schleyer, P. V. R., Murty, T. S. S. R. & Robinson, L., *Tetrahedron*, **20** (1964), 1635; Krueger, P. J. & Mettee, H. D., *Can. J. Chem.*, **43** (1965), 2888; Rao, C. N. R., cited in *The chemistry of nitro and nitroso groups*, Part I, edited by H. Feuer (Interscience Publishers Inc., New York), 1969, 114.
4. Calus, H., Jankowska, H., Piotrowska, H. & Urbanski, T., *Chemy Ind.*, (1959), 1286.
5. Rossmy, G., *Chem. Ber.*, 88 (1955), 1969.
6. Brown (Jr), J. F., *J. Am. chem. Soc.*, **77** (1955), 6341.
7. Pristera, F., Halik, M., Castelli, A. & Fredericks, W., *Analyt. Chem.*, **32** (1960), 495.
8. Urbanski, T. & Witanowski, M., *Trans. Faraday Soc.*, **59** (1963), 1046.
9. Urbanski, T. & Witanowski, M., *Trans. Faraday Soc.*, **59** (1963), 1039.
10. Mortimer, C. T., Spedding, H. & Springall, H. D., *J. chem. Soc.*, (1957), 188.
11. Buczkowskii, Z., Piotrowska, H. & Urbanski, T., *Bull. Acad. pol. Sci., Sér. chim.*, **11** (1963), 197.
12. Hetnarski, B., Poludnikiewicz, W. & Urbanski, T., *Tetrahedron Lett.*, (1970), 3; *Bull. Acad. pol. Sci., Sér. chim.*, **18** (1970), 385.
13. Urbanski, T., Hetnarski, B. & Poludnikiewicz, W., *Bull. Acad. pol. Sci., Sér. chim.*, **18** (1970), 405.
14. Urbanski, T., Hetnarski, B. & Poludnikiewicz, W., *Can. J. Chem.*, **50** (1972), 3340.
15. Corey, E. J. & Sneen, R. A., *J. Am. chem. Soc.*, **77** (1955), 2505.
16. Urbanski, T., Gurne, D., Kolinski, R., Piotrowska, H., Janczyk, A., Serafin, B., Szretter-Szmid, M. & Witanowski, M., *Tetrahedron*, (*Suppl.* 1), **20** (1964), 195.
17. Kedzierski, B., Piotrowska, H. & Urbanski, T., *Chemy Ind.*, (1971), 1302.
18. Eliel, E. L., *Angew. Chem. intern. Edn*, **11** (1972), 739.
19. Kedzierski, B., Piotrowska, H. & Urbanski, T., *Bull. Acad. pol. Sci., Sér. chim.*, **19** (1971), 177.
20. Kedzierski, B., Piotrowska, H. & Urbanski, T., *Roczn. Chem.*, **46** (1972), 1559.
21. Piotrowska, H., Serafin, B. & Urbanski, T., *Tetrahedron*, **19** (1963), 379.
22. Hirst, E. L., Jones, J. K. N., Minahan, S., Ochynski, T. W., Thomas, A. T. & Urbanski, T., *J. chem. Soc.*, (1947), 924; Urbanski, T. & Gürne, D., *Roczn. Chem.*, **28** (1954), 175; **31** (1951), 869; Urbanski, T. & Piotrowska, H., *Roczn. Chem.*, **29** (1955), 379; Urbanski, T. & Kolesinska, J., *Roczn. Chem.*, **29** (1955), 392; Urbanski, T., Dabrowska, H., Lesiowska, B. & Piotrowska, H., *Roczn. Chem.*, **31** (1957), 687; Eckstein, Z., Gluzinski, P., Grochowski, E., Mordarski, M. & Urbanski, T., *Bull. Acad. pol. Sci., Sér. chim.*, **10** (1962), 331.
23. Gürne, D. & Urbanski, T., *J. chem. Soc.*, (1959), 1912.
24. Chylinska, J. B. & Urbanski, T., *J. Heteroc. Chim.*, **1** (1964), 93.
25. Gürne, D., Stefaniak, L., Urbanski, T. & Witanowski, M., *Tetrahedron*, (*Suppl.* 1), **20** (1964), 211.
26. Gürne, D., Urbanski, T., Witanowski, M., Karniewska, B. & Stefaniak, L., *Tetrahedron*, **20** (1964), 1173.
27. Szretter-Szmid, M. & Urbanski, T., *Tetrahedron Lett.*, (1967), 2131.
28. Malinowski, S. & Urbanski, T., *Roczn. Chem.*, **25** (1951), 183; Urbanski, T. & Lipska, E., *Roczn. Chem.*, **26** (1952), 182; Urbanski, T., Biernacki, Z. & Lipska, E., *Roczn. Chem.*, **28** (1954), 169; Urbanski, T. & Piotrowska, H., *Roczn. Chem.*, **29** (1955), 329.
29. Piotrowska, H. & Urbanski, T., *J. chem. Soc.*, (1962), 1942.
30. Eliel, E. L., Hutchins, R. O. & Kopp, L. D., *J. Am. chem. Soc.*, **90** (1968), 7174.
31. Katritzky, A. R., Jones, R. A. Y. & Snarey, M., *J. chem. Soc.*, (*B*) (1970), 131.
32. Urbanski, T., *Chemistry and technology of explosives*, Vol. III (Pergamon Press Ltd, Oxford), 1967.
33. Stefaniak, L., Urbanski, T., Witanowski, M. & Januszewski, H., *Roczn. Chem.*, **43** (1969), 1687.
34. Looney, C. E., Phillips, W. D. & Reilly, E. L., *J. Am. chem. Soc.*, **79** (1957), 6136; Blears, D. J., *J. chem. Soc.*, (*Suppl.* 2) (1964), 6256.