STEREOCHEMISTRY OF HETEROCYCLIC SYSTEMS DERIVING FROM PRIMARY NITROALKANES

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Abstract—The conformation of tetrahydro-1,3-oxazine, 1,3-dioxane and hexahydropyrimidine derivatives containing nitro group in the 5-position, and 3,7-dinitro-1,5-diazacyclooctane derivatives was investigated. Dipole moments of these compounds were measured and compared with the values calculated for the theoretically possible conformations. N.M.R. spectra of some compounds were also measured. The results are discussed.

INTRODUCTION

OUR work on conformation of compounds with heterocyclic non aromatic rings started in 1956. The following are the ring systems so far examined and partly described in our published papers:

> hexahydropyrimidine,
> 1,5-diazacyclo-octane,
> 1,5-diazabicyclo(3.3.3)undecane,
> tetrahydro-1,3-oxazine,
> 1,3-dioxane,
> 2-bora-1,3-dioxane and
> 2-sila-1,3-dioxane.

All the examined compounds are derivatives of primary nitroalkanes and the starting substances for their preparation are 2-alkyl-2-nitropropane-1,3-diols. The structure of the compounds was confirmed by examination of I.R. spectra, dipole moments and, more recently, N.M.R. spectra.

The main method of establishing the conformation consisted in measuring and calculating the dipole moments of the compounds. The method is particularly suited to investigate the conformation of nitro compounds. Thanks to the high dipole moment of the nitro group ($\mu = 3 \cdot 5$ D), various conformations produce fairly high change of the dipole moment value. Hence it was relatively easy to choose the most probable conformation. The following were the principles

adopted in the calculation of dipole moments: (1)—a stereo-model (Dreiding and Stuart-Briegleb models) was built for a given conformation, (2)—the exact positions of the atoms and directions of the interatomic bonds were calculated, by means of vector analysis, (3)—the theoretical dipole moment was calculated for each conformation. Then the dipole moment was measured and the calculated and experimental values were compared.

Recently, N.M.R. spectra were used to establish the conformation of derivatives of tetrahydro-1,3-oxazine.

EXPERIMENTAL

5-Alkyl-5-nitro-tetrahydro-1,3-oxazines (I) were prepared from the corresponding 2-alkyl-2-nitropropane-1,3-diols by heating with formaldehyde and primary amines.[1,2]

5-Alkyl-5-nitro-1,3-dioxanes (II) were prepared from 2-alkyl-2-nitropropane-1,3-diols by heating with aldehydes or ketones in the presence of a catalytic quantity of p-toluenesulphonic acid.[3]

5-Alkyl-5-nitro-2-bora-1,3-dioxanes (IV) were obtained by esterification of 2-alkyl-2-nitropropane-1,3-diols with phenylboronic acid.[4]

2,2-Dimethyl-5-alkyl-5-nitro-2-sila-1,3-dioxanes (VIII) were prepared by heating 2-alkyl-2-nitropropane-1,3-diols with dimethyldiacetoxysilane.[5]

5-Alkyl-5-nitro-hexahydropyrimidines (IX),[6,7] 3,7-dialkyl-3,7-dinitro-1,5-diaza-cyclo-octanes (X)[7] and 3,7,10-trialkyl-3,7,10-trinitro-1,5-diazabicyclo(3.3.3)unde-canes (XI)[7] were obtained by heating 2-alkyl-2-nitropropane-1,3-diols with an excess of ammonia or primary amine.

[1] E. L. Hirst, J. K. N. Jones, S. Minahan, F. W. Ochyński, A. T. Thomas and T. Urbański, J. Chem. Soc. 924 (1947); T. Urbański and D. Gürne, Roczniki Chem. 28, 175 (1954); 31, 855, 869 (1957); T. Urbański and H. Piotrowska, ibid. 29, 379 (1955); Bull. Acad. Polon. Sci., Cl. III 3, 389 (1955); T. Urbański and J. Kolesińska, Roczniki Chem. 29, 392 (1955); T. Urbański, H. Dąbrowska, B. Lesiowska and H. Piotrowska, ibid. 31, 687 (1957); D. Gürne and T. Urbański, unpublished results.

[2] Z. Eckstein, P. Gluziński, W. Hofman and T. Urbański, J. Chem. Soc. 489 (1961).

[3] S. Malinowski and T. Urbański, Roczniki Chem. 25, 183 (1951); Z. Eckstein and T. Urbański, ibid. 30, 1163, 1175 (1956); H. Piotrowska and T. Urbański, unpublished results.

[4] H. Piotrowska, B. Serafin and T. Urbański, Tetrahedron 19, 379 (1963).

[5] T. Urbański and M. Szretter-Szmid, Symposium on Nitro Compounds, Abstracts p. 122, Warsaw (1963).

[6] S. Malinowski and T. Urbański, Roczniki Chem. 25, 183 (1951); T. Urbański, and J. Kolesińska, ibid. 29, 392 (1955); H. Piotrowska and T. Urbański, J. Chem. Soc. 1942 (1962).

[7] T. Urbański and E. Lipska, Roczniki Chem. 26, 182 (1952); T. Urbański, Z. Biernacki and E. Lipska, ibid. 28, 169 (1954); T. Urbański and H. Piotrowska, ibid. 29, 379 (1955); J. K. N. Jones, R. Koliński, H. Piotrowska and T. Urbański, ibid. 31, 101 (1957); Bull. Acad. Polon. Sci., Cl. III 4, 521 (1956).

Dipole moments were measured by the heterodyne beat method with a Dipolmeter Type DM 01 (WTW Weilheim). The calculation was done by the extrapolation method of Le Fèvre and Vine. All substances were examined as solutions in carbon tetrachloride at 20°. The experimental error was of the order of ±0·1 D.

Dipole moments were calculated by using the values for dipole moments of separate bonds and of the nitro group and the bond lengths as collected in Table 1.

TABLE 1. DIPOLE MOMENTS AND BOND LENGTHS

Bond	Dipole moment μ, D	Bond length Å
C—C	0	1·54
C—O	0·86	1·43
C—N	0·45	1·47
N—H	1·31	1·00
B—O	0·4	1·54
B—C	0·25	1·58
O—Si	0·95	1·66
Si—C	0·2	1·89
NO$_2$	3·5	

The valency angles are given in Table 2.

TABLE 2. VALENCY ANGLES

Ring	Bond	Angle	Bond	Angle	Bond	Angle
Tetrahydro-1,3-oxazine	C—O—C	110°42′	O—C—N	109°28′	C—N—C	111°
1,3-Dioxane	C—O—C	110°	O—C—O	109°28′		
2-Bora-1,3-dioxane	B—O—C	115°	O—B—O	117°	O—B—C	121°30′
2-Sila-1,3-dioxane	C—Si—C	106°	O—Si—O	115°	O—Si—C	113°
	Si—O—C	110°42′				
Hexahydropyrimidine	C—N—C	110°	N—C—N	109°28′		

Angle C—N—C in 1,5-diazacyclo-octane and 1,5-diazabicyclo(3.3.3)undecane was taken as 110°.

Angles C—C—C and C—C-heteroatom were taken as 109°28′ for all compounds.

N.M.R. spectra were taken by means of Varian V-4300C spectrometer at 60 Mc and 27°.

Infra red spectra were determined with a Hilger H-800 double-beam spectrophotometer with sodium chloride or lithium fluoride optics.

DISCUSSION

Derivatives of 5-nitro-tetrahydro-1,3-oxazine[8]

5-Nitro-tetrahydro-1,3-oxazine derivatives of general formula I were examined. Unsubstituted tetrahydro-1,3-oxazine ring can exist in four forms: one chair (IA) and three boat forms (IB, IC and ID).
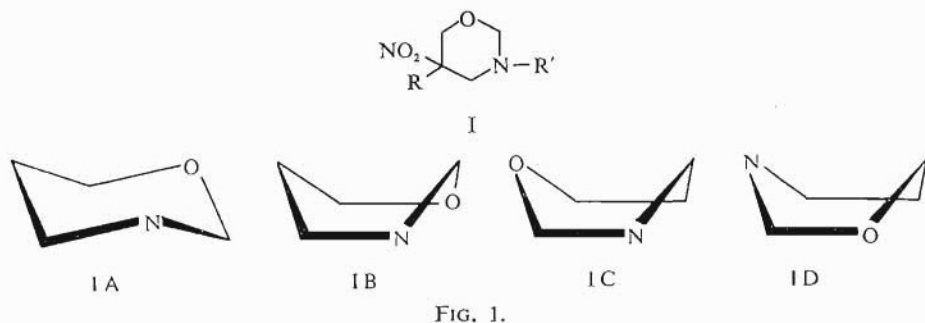

I

I A   I B   I C   I D

FIG. 1.

The presence of a nitro group in position 5 and of the group R' attached to the ring nitrogen makes four conformations possible for each ring form. The four conformations of chair form (IA) and one of the boat form (ID) are given in Fig. 2.

I A₁   I A₂   I A₃

I A₄   I D₃
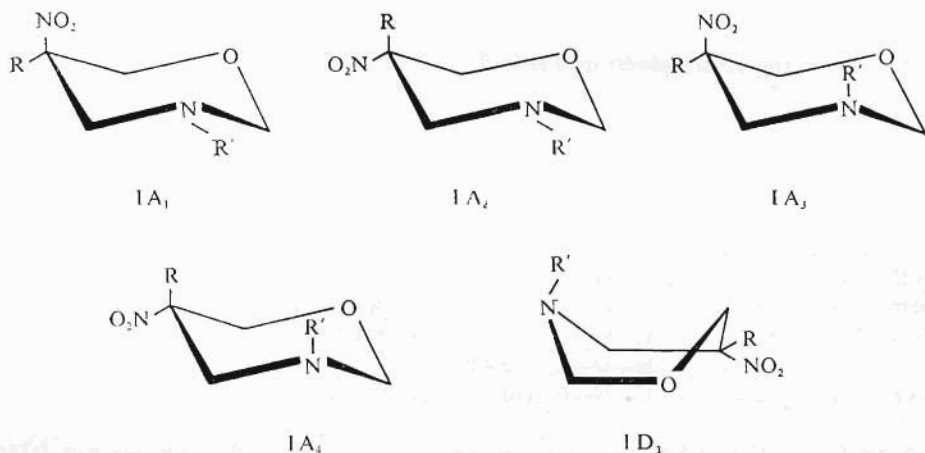
FIG. 2.

The calculated dipole moments for all 16 conformations are collected in Table 3. The measured dipole moment values are given in Table 4.

All substances examined can be divided into four groups depending on their dipole moment values.

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[8] D. Gürne and T. Urbański, *J. Chem. Soc.* 1912 (1959); D. Gürne and T. Urbański, *Roczniki Chem.* **34**, 881 (1960).

TABLE 3. CALCULATED DIPOLE MOMENTS OF 5-ALKYL-5-NITRO-TETRAHYDRO-1,3-OXAZINES (I)[9]

Conformation	NO_2	R'	R'=alkyl μ,D	R'=H μ,D
IA_1	a	e	4·59	5·01
IA_2	e	e	2·98	3·58
IA_3	a	a	3·97	3·14
IA_4	e	a	2·80	3·14
IB_1	fp	be	3·19	
IB_2	bs	be	2·98	
IB_3	fp	ba	3·65	
IB_4	bs	ba	2·80	
IC_1	ba	be	3·01	
IC_2	be	be	3·59	
IC_3	ba	ba	2·42	
IC_4	be	ba	3·73	
ID_1	ba	bs	3·85	
ID_2	be	bs	3·32	
ID_3	ba	fp	3·98	
ID_4	be	fp	2·80	

TABLE 4. EXPERIMENTAL VALUES OF DIPOLE MOMENTS
OF 5-ALKYL-5-NITRO-TETRAHYDRO-1,3-OXAZINES (I)

R	R'	μ,D
CH_3	$t\text{-}C_4H_9$	4·53
CH_3	C_6H_{11}	4·45
C_2H_5	C_6H_{11}	4·42
$n\text{-}C_3H_7$	C_6H_{11}	4·41
$iso\text{-}C_3H_7$	C_6H_{11}	4·56
$n\text{-}C_4H_9$	C_6H_{11}	4·46
CH_3	CH_3	4·02
CH_3	C_2H_5	3·95
CH_3	$n\text{-}C_4H_9$	4·04
CH_3	$CH_2C_6H_5$	4·12
$n\text{-}C_3H_7$	$n\text{-}C_4H_9$	4·04
C_2H_5	H	3·70
H	CH_3	3·42
H	$CH_2C_6H_5$	3·36

C_6H_{11} = cyclohexyl.

Group 1. Compounds I with substituents R from CH_3 to $n\text{-}C_4H_9$ and bulky $R' = t\text{-}C_4H_9$, cyclohexyl. The measured dipole moment, 4·41–4·56 D, cor-

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[9] Notation of the conformations of the substituents in the hetero-rings is the same as used for cyclohexane. In the case of the boat forms, the notation is that of K. Klyne, *Progress in Stereochemistry*, vol. I, p. 78. Butterworths, London (1954).

responds to conformation IA_1, i.e. the nitro, R and R' group is axial, equatorial, and equatorial, respectively. The measured dipole moments are slightly lower than the calculated ones, but the deviation is so small that the other conformations should be excluded.

The N.M.R. spectrum for substance I ($R = CH_3$, $R' = t\text{-}C_4H_9$) was also examined.[10] No conversion of the ring was found. The interpretation of this spectrum gives a full support for the conformation IA_1 determined by the dipole moments measurement.

Group 2. Compounds I with substituents: $R = CH_3$ and $n\text{-}C_3H_7$; $R' = CH_3$, C_2H_5, $n\text{-}C_4H_9$ and $CH_2C_6H_5$. The measured dipole moments are $3 \cdot 95$–$4 \cdot 12$ D. They can correspond to conformations IA_3, ID_1, or ID_3.

The N.M.R. spectrum of compound I ($R = CH_3$, $R' = CH_3$) favours conformation IA_3.[10]

The axial position of the nitro group and simultaneously of the substituent R' seems to be surprising. However, the agrement between dipole moment measurement and N.M.R. spectrum appears to give sufficient support to assume conformation IA_3.

Group 3. Compound I ($R = C_2H_5$, $R' = H$) gave the dipole moment value $3 \cdot 70$ D[11], very near to the value calculated for conformation IA_2 ($3 \cdot 58$ D, Table 3).

The N.M.R. spectrum[10] of compound I ($R = C_2H_5$, $R' = H$) is similar to this of the compound I ($R = CH_3$, $R' = t\text{-}C_4H_9$). No conversion of the ring seems to occur and the nitro group is axial, hence both conformations IA_1 or IA_3 could be accepted. No definite determination can be made of the position of the hydrogen atom attached to the ring nitrogen.

Group 4. A characteristic feature of this group of compounds I is that they contain a secondary nitro group ($R = H$). When R' was CH_3 and $CH_2C_6H_5$ the dipole moments were $3 \cdot 42$ D and $3 \cdot 36$ D, respectively. It was impossible to assign any of here recorded conformations on the basis of the dipole moments only.

The N.M.R. spectra,[10] however, indicate a ring conversion. Accordingly, the dipole moment would acquire an intermediate value.

Quaternary salts of 3,5-dialkyl-5-nitro-tetrahydro-1,3-oxazines[12]

These salts were also obtained and it was shown that diastereoisomeric pairs can be formed when two substituents attached to the ring nitrogen are different.

[10] G. Gürne, L. Stefaniak, T. Urbański and M. Witanowski, *This Supplement* p. 211.
[11] D. Gürne, unpublished results.
[12] D. Gürne, T. Urbański and M. Witanowski, *XXII-nd IUPAC Congress, Abstracts* A3-51. London (1963); D. Gürne, T. Urbański, M. Witanowski, B. Karniewska and L. Stefaniak, *Tetrahedron* **20**, 1173 (1964).

One of the pairs of the isomers: 3,5-dimethyl-3-ethyl-5-nitro-tetrahydro-1,3-oxazinium iodides (II), was examined in N.M.R. spectrometer in a D_2O solution.
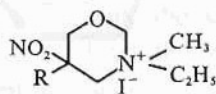
II

The spectra showed clearly the conformations of N-methyl groups in the two isomers to be different. Taking into consideration that nitro group and $R' = CH_3$ are axial (as formerly assumed[10]), the equatorial ethyl would be introduced into position 3 (conformation IIA_1) by adding ethyl iodide to oxazine I $(R = CH_3, R' = CH_3)$ to form II. When I $(R = CH_3, R' = C_2H_5)$ reacted with methyl iodide the ethyl group remained axial and the methyl group assumed the equatorial position (conformation IIA_2). All this is valid provided no changes in positions of substituents occur during the quaternization.
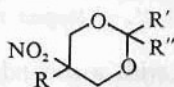

IIA_1 IIA_2
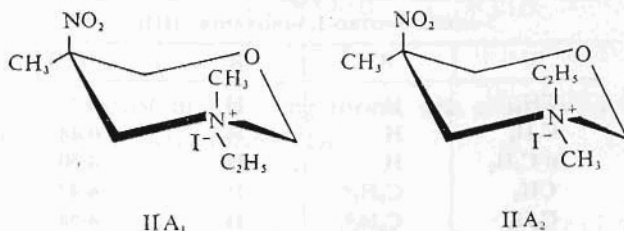
FIG. 3.

Derivatives of 5-nitro-1,3-dioxane[13]

Conformation was established for a number of 5-nitro-1,3-dioxane derivatives of the general formula III. Unsubstituted 1,3-dioxane ring can exist in three

III

forms: one chair (IIIA) and two boat forms (IIIB and C). For each form two conformations can theoretically exist, depending on the axial or equatorial arrangement of the nitro group. The alkyl or phenyl in the 2-position does not influence the value of the dipole moment. Six characteristic conformations are, therefore, possible. The calculated dipole moments are given in Fig. 4. The measured values are collected in Table 5.

Two groups of 5-nitro-1,3-dioxanes (III) can be distinguished.

Group 1— is characterised by high dipole moments, 4·43–4·58 D. All compounds III with $R = CH_3$, C_2H_5 and n-C_3H_7 belong to this group. The dipole moment values are very close to the data calculated for the conformation $IIIA_1$.

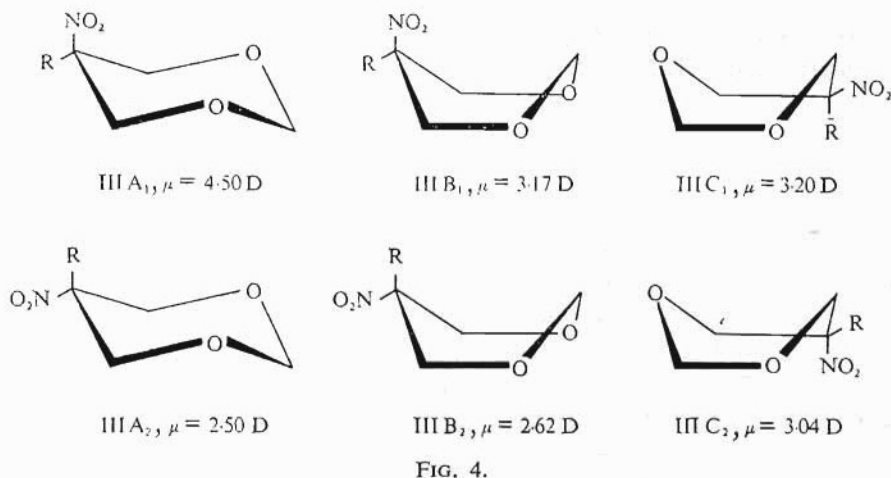[13] H. Piotrowska, unpublished results.

III A_1, $\mu = 4.50$ D   III B_1, $\mu = 3.17$ D   III C_1, $\mu = 3.20$ D

III A_2, $\mu = 2.50$ D   III B_2, $\mu = 2.62$ D   III C_2, $\mu = 3.04$ D

Fig. 4.

TABLE 5. Experimental values of dipole moments of 5-alkyl-5-nitro-1,3-dioxanes (III)

R	R'	R''	μ,D
CH_3	H	H	4·45
C_2H_5	H	H	4·48
n-C_3H_7	H	H	4·50
CH_3	$C_6H_5{}^a$	H	4·47
C_2H_5	$C_6H_5{}^b$	H	4·58
CH_3	CH_3	CH_3	4·43
C_2H_5	CH_3	CH_3	4·47
n-C_3H_7	CH_3	CH_3	4·55
H	H	H	2·65
H	CH_3	CH_3	2·45

[a] Isomer m.p. 121–2°.   [b] Isomer m.p. 74–5°.

Group 2. The compounds III with a secondary nitro group (R = H) belong to this group. They are characterised by low dipole moments, 2·65 and 2·45 D, which correspond to conformations IIIA$_2$ and IIIB$_2$. So far it is impossible to decide which of these two conformations should be assigned to compounds III (R = H). N.M.R. spectra are now in progress to find a definitive answer.

Derivatives of 5-nitro-2-bora-1,3-dioxane[14]

Derivatives of 5-nitro-2-phenyl-2-bora-1,3-dioxane (IV) were investigated. No
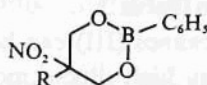
IV

[14] T. Urbański, B. Serafin, H. Piotrowska and A. Jończyk, *Symposium on Nitro Compounds, Abstracts*, p. 120, Warsaw (1963).

analogy with cyclohexane can here be drawn because of the presence of the boron atom in the ring. It is well known that all three covalent bonds of boron lie in one plane. It was necessary to begin with calculating and measuring dipole moment of the simpliest compound with the same ring 2-phenyl-2-bora-1,3-dioxane (V). This enabled us to establish the value and the direction of the dipole moment of the compound V.
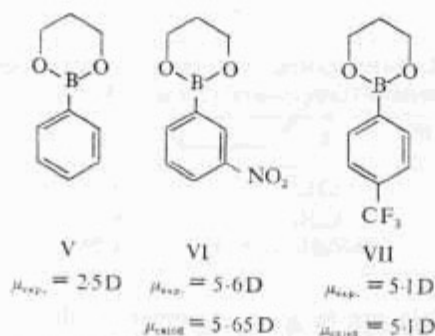

V
$\mu_{exp.} = 2.5\,D$

VI
$\mu_{exp.} = 5.6\,D$
$\mu_{calca} = 5.65\,D$

VII
$\mu_{exp.} = 5.1\,D$
$\mu_{calca} = 5.1\,D$

FIG. 5.

Compound V can exist in four ring forms: one chair (VA) two boat (VB and C) and one "semi planar" form (VD).

VA, $\mu = 1.9\,D$ VB, $\mu = 1.9\,D$ VC, $\mu = 1.8\,D$ VD, $\mu = 2.5\,D$
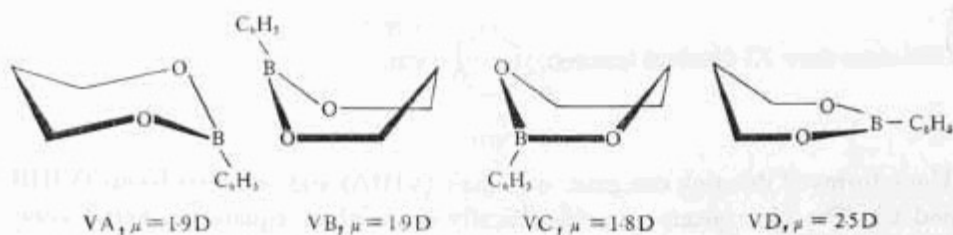
FIG. 6.

The measured dipole moment of compound V was found to be 2·5 D. This corresponds to conformation VD. The moment is directed along the bond B—C. However, the difference is very small between dipole moments of conformation VD and the others (ca. 0·6 D). Therefore it was necessary to examine a few more derivatives of V, particularly those with such a substituent in the aromatic ring which would increase the dipole moment. Therefore, dipole moments of 2-(m-nitrophenyl)- and 2-(p-trifluormethylphenyl)-2-bora-1,3-dioxane (compounds VI and VII, respectively) were measured. The values obtained were in agreement with conformation VD. Accordingly, conformation VD was accepted as the basis for the conformation of 5-nitro-2-phenyl-2-bora-1,3-dioxane derivatives (IV).

Dipole moments calculated for two conformations are given in Fig. 7. Measured dipole moments are collected in Table 6.
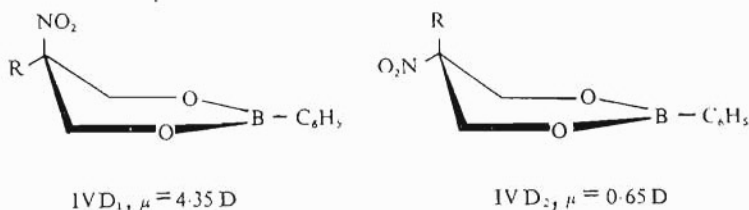
IV D$_1$, μ = 4·35 D   IV D$_2$, μ = 0·65 D

Fig. 7.

TABLE 6. EXPERIMENTAL VALUES OF DIPOLE MOMENTS OF
2-PHENYL-5-ALKYL-5-NITRO-2-BORA-1,3-DIOXANES (IV)

R	μ,D
CH$_3$	4·25
C$_2$H$_5$	4·18
n-C$_3$H$_7$	4·20

The experimental data are in good agreement with conformation IVD$_1$, and this was assumed as the most probable conformation of compounds IV.

Derivatives of 5-nitro-2-sila-1,3-dioxane[15]

Derivatives of 2,2-dimethyl-5-nitro-2-sila-1,3-dioxane (VIII) were investigated.
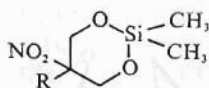
VIII

Three forms of this ring can exist: one chair (VIIIA) and two boat forms (VIIIB and C). The nitro group can theoretically be axial or equatorial, hence compounds VIII can exist in six conformations. Calculated dipole moments are given in Fig. 8.

Measured values of dipole moments are collected in Table 7.

TABLE 7. EXPERIMENTAL VALUES OF DIPOLE MOMENTS
OF 2,2-DIMETHYL-5-ALKYL-5-NITRO-2-SILA-1,3-DIOXANES (VIII)

R	μ,D
CH$_3$	3·30
C$_2$H$_5$	3·36
n-C$_3$H$_7$	3·45
n-C$_4$H$_9$	3·48
n-C$_5$H$_{11}$	3·55

[15] T. Urbański and M. Szretter-Szmid, *Symposium on Nitro Compounds, Abstracts* p. 122, Warsaw (1963).

VIII A$_1$, μ = 4·63 D   VIII B$_1$, μ = 3·36 D   VIII C$_1$, μ = 5·53 D

VIII A$_2$, μ = 2·57 D   VIII B$_2$, μ = 2·57 D   VIII C$_2$, μ = 4·71 D

FIG. 8.
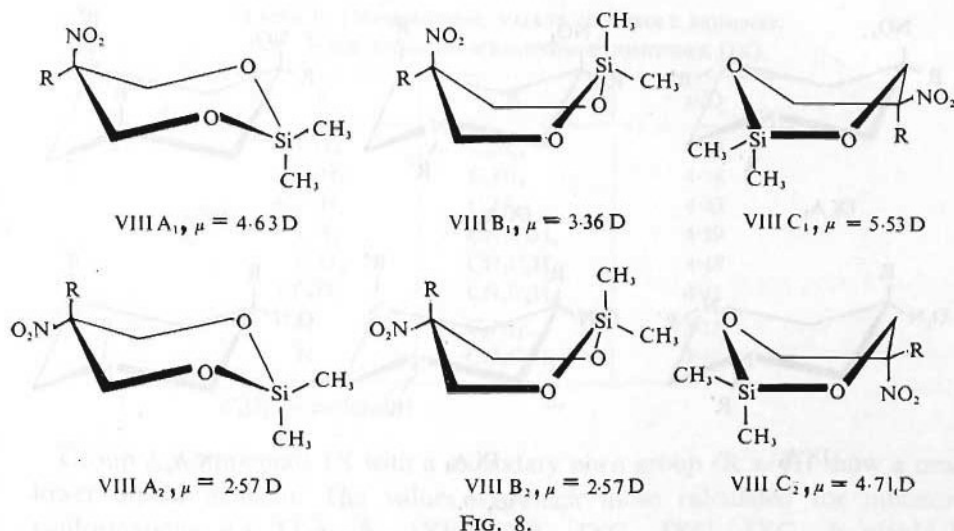
The experimental data correspond either to conformation VIIIB$_1$ or to mean value for two conformations VIIIA$_1$ and VIIIA$_2$. Further experiments are now in progress to elucidate which conformation should be assigned to compounds VIII.

Derivatives of hexahydropyrimidine[16]

5-Nitro-hexahydropyrimidine derivatives of general formula IX were examined.
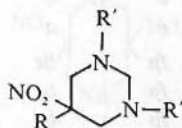
IX

Hexahydropyrimidine ring can exist in three characteristic forms: one chair (IXA) and two boat forms (IXB and C). The nitro group can be axial or equatorial and substituents R' can be in three or four positions relative to each other. Thus six conformations are possible in the instance of IXA and IXB forms and eight in form IXC. All conformations of form IXA are presented in Fig. 9.

Dipole moments calculated for all twenty conformations are collected in Table 8.

Experimental values of dipole moments are given in Table 9.

5-Nitro-hexahydropyrimidines (IX) can be classified into two groups according to the value of their dipole moments.

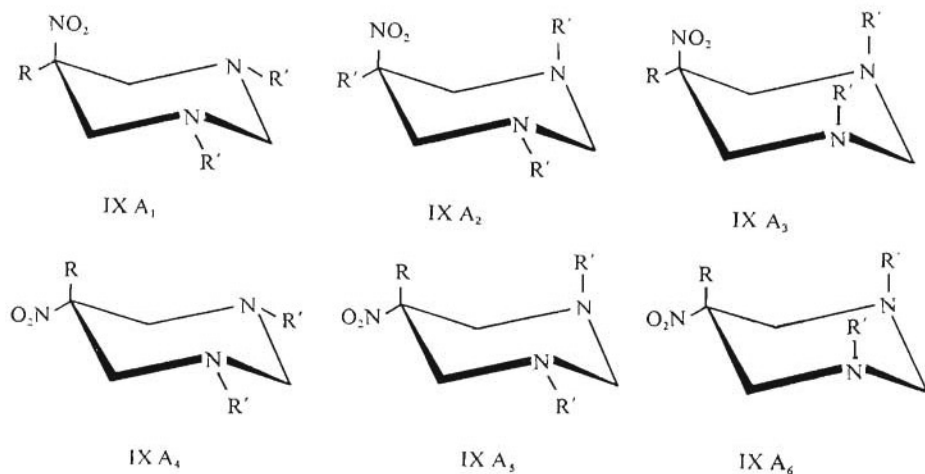[16] H. Piotrowska and T. Urbański, *J. Chem. Soc.* 1942 (1962).

FIG. 9.

TABLE 8. CALCULATED DIPOLE MOMENTS OF
5-ALKYL-5-NITRO-HEXAHYDROPYRIMIDINES (IX)[9]

Conformation	NO_2	R'	R'	μ,D
IXA$_1$	a	e	e	4·35
IXA$_2$	a	e	a	3·72
IXA$_3$	a	a	a	3·10
IXA$_4$	e	e	e	3·12
IXA$_5$	e	e	a	3·04
IXA$_6$	e	a	a	3·06
IXB$_1$	fp	be	be	2·55
IXB$_2$	fp	be	ba	3·19
IXB$_3$	fp	ba	ba	3·70
IXB$_4$	bs	be	be	3·07
IXB$_5$	bs	be	ba	2·91
IXB$_6$	bs	ba	ba	2·82
IXC$_1$	be	bs	be	3·27
IXC$_2$	be	fp	be	2·94
IXC$_3$	be	bs	ba	3·45
IXC$_4$	be	fp	ba	3·01
IXC$_5$	ba	bs	be	3·31
IXC$_6$	ba	fp	be	3·64
IXC$_7$	ba	bs	ba	2·76
IXC$_8$	ba	fp	ba	2·94

Group 1. Compounds IX (R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$; R' = cyclohexyl CH$_2$C$_6$H$_5$) are characterised by high dipole moments which indicate conformation IXA$_1$.

TABLE 9. EXPERIMENTAL VALUES OF DIPOLE MOMENTS
OF 5-ALKYL-5-NITRO-HEXAHYDROPYRIMIDINES (IX)

R	R′	μ,D
CH_3	C_6H_{11}	4·43
C_2H_5	C_6H_{11}	4·36
$n\text{-}C_3H_7$	C_6H_{11}	4·43
CH_3	$CH_2C_6H_5$	4·39
C_2H_5	$CH_2C_6H_5$	4·45
$n\text{-}C_3H_7$	$CH_2C_6H_5$	4·41
H	C_6H_{11}	3·15
H	$CH_2C_6H_5$	3·18

C_6H_{11} = cyclohexyl.

Group 2. Compounds IX with a secondary nitro group (R = H) show a much lower dipole moment. The values approach those calculated for numerous conformations, e.g. IXA$_3$–A$_6$, IXB$_2$, IXB$_4$, IXC$_1$, IXC$_4$, IXC$_5$. It would be difficult to draw any definite conclusion, although on the basis of our knowledge of such systems conformation IXA$_4$ seems to be more probable than others, considering that NO$_2$ would preferentially be equatorial, whereas hydrogen atom is axial.

Derivatives of 3,7-*dialkyl*-3,7-*dinitro*-1,5-*diazacyclo-octane*[17]

3,7-Dinitro-1,5-diazacyclo-octane derivatives of general formula X were

NO$_2$ ... NR′ ... NO$_2$
R ... R
NR′

X
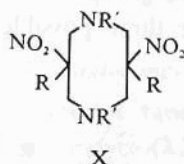
examined. It is well known that cyclo-octane can theoretically exist in at least seven ring forms. Substitution with nitrogen atoms at positions 1 and 5 increased the number of the forms to several dozens. The substitution of the 1,5-diazacyclo-octane ring with two nitro groups and two alkyls at positions 3 and 7 reduces the number of possible forms of the ring to three only, as all other are impossible for steric reasons. This can be predicted by using the atomic models. These three forms are presented on Fig. 10.

Further restriction of possible ring forms can be achieved on the basis of X-ray investigation of medium size rings by Dunitz, Prelog and their co-workers.[18] They established that in hydrobromide of azacyclo-octane the eight-

[17] R. Koliński, H. Piotrowska and T. Urbański, *J. Chem. Soc.* 2319 (1958); *Roczniki Chem.* **32**, 1289 (1958).
[18] J. D. Dunitz and V. Prelog, *Angew. Chem.* **72**, 896 (1960).

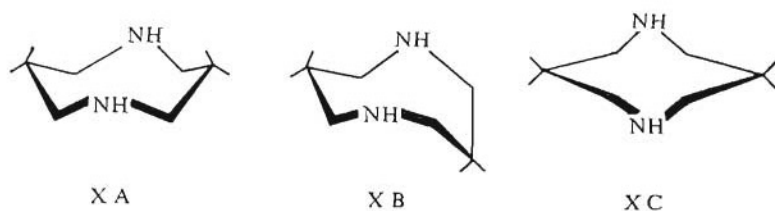X A   X B   X C

FIG. 10.

membered ring exists in the "crown" form. They advanced a hypothesis that medium size ring possesses a stable ring form. The stability is dictated by low energy of the forms. They did not change even on passing from the solid to the molten state. Other authors[19] also found that the crown form is the best to explain the properties of the eight-membered ring. However a deformation of the crown form is also possible.

Eventually we accepted crown form (XA). The presence of nitro groups in the positions 3 and 7 creates the possibility of the existence of *cis* and *trans* isomers. Two conformations *aa* and *ee* for *cis* isomer and one *ae* for *trans* isomer are possible.[20]

Examination of infra red absorption spectra of dilute solutions of the compounds X with secondary amino group ($R' = H$) shows that an internal hydrogen bond is very probable. This was established by means of molecular models to be possible when one of the hydrogens of secondary amino groups occupies an axial position. It can be bonded with nitrogen atom of another amino group or with an axial nitro group.

Dipole moments calculated for three possible conformations with ring form XA are given in Fig. 11.

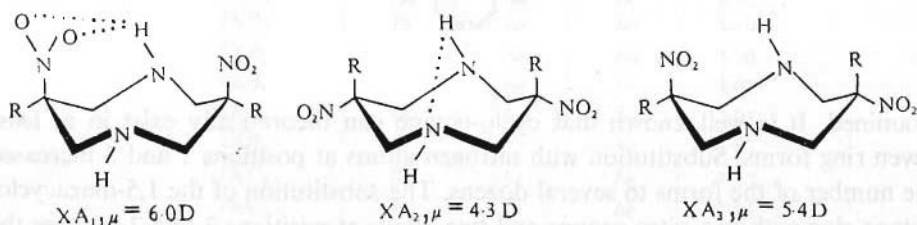$XA_1, \mu = 6.0D$ $XA_2, \mu = 4.3D$ $XA_3, \mu = 5.4D$

FIG. 11.

The measured dipole moments are collected in Table 10.

It can be seen that 3,7-dialkyl-3,7-dinitro-1,5-diazacyclo-octanes (X) with higher dipole moments, 5.4–5.5 D, possess conformation XA_3, i.e. they are

[19] N. L. Allinger, S. P. Jindal and M. A. Da Rooge, *J. Org. Chem.* **27**, 4290 (1962) and literature cited therein.

[20] The notation *a* for axial and *e* for equatorial are used by analogy with cyclohexane. They are not exactly the same in eight-membered rings where the terms quasiaxial (a') and quasiequatorial (e') should be applied.

TABLE 10. EXPERIMENTAL VALUES OF DIPOLE MOMENTS
OF 3,7-DIALKYL-3,7-DINITRO-1,5-DIAZACYCLO-OCTANES (X)

R	R'	m.p.°C	μ,D
CH_3	H	114—115	5·5
CH_3	H	128—129	4·4
C_2H_5	H	63—64	5·4
C_2H_5	H	94—95	4·6
n-C_3H_7	H	73—74	5·5
n-C_3H_7	H	89—90	4·5
n-C_3H_7	CH_3	49—50	4·2

trans isomers. Those with lower dipole moments, 4·4–4·6 D, have conformation
XA_2, i.e. they are *cis* isomers. In this instance the nitro groups are in the
equatorial positions.

In the instance of X (R = n-C_3H_7, R' = CH_3),[21] the dipole moment was
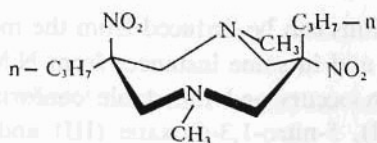calculated to be 4·1 D for the conformation depicted in Fig. 12 and the observed

FIG. 12.

value was 4·2 D. Thus the nitro groups and methyl radicals are in *trans* (*ae*)
and *cis* (*ee*) positions, respectively.

Derivatives of 1,5-diazabicyclo(3.3.3)undecane[17]

Compounds with two fused diazacyclooctane rings were examined: they were
3,7,10-trialkyl-3,7,10-trinitro-1,5-diazabicyclo(3.3.3)undecanes (XI). Molecular
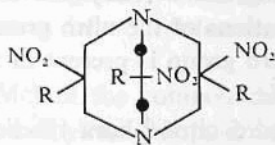
XI

models show that the compounds can exist in one ring form only. Two conforma-
tions of nitro groups are possible: symmetric and asymmetric.

Calculated dipole moments of symmetric and asymmetric conformations XIA_1
and XIA_2 are 0·0 D and 5·5 D, respectively.

Experimental values were: XI, R = C_2H_5, $\mu = 5·7$ D and XI, R = n-C_3H_7,
$\mu = 5·6$ D. These values correspond to asymmetric conformation XIA_2.

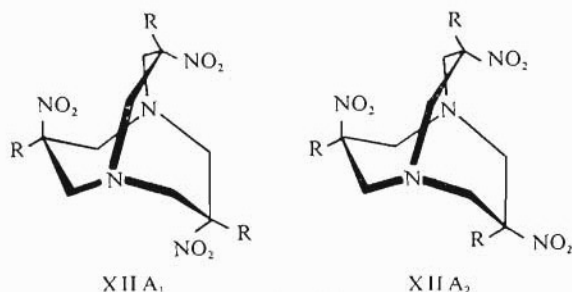[21] H. Piotrowska, unpublished results.

XII A₁   XII A₂

FIG. 13.

A chemical argument in favour of the asymmetric structure of the examined compounds XI was its hydrolysis with hydrochloric acid which yielded both isomeric 3,7-dialkyl-3,7-dinitro-1,5-diazacyclooctanes (X, R = C_2H_5 and n-C_3H_7).

CONCLUSIONS

A few general conclusions can be deduced from the measurement and calculations of dipole moments and in some instances from N.M.R. spectra.

(1) No ring conversion occurs and the stable conformation exists in 5-nitro-tetrahydro-1,3-oxazine (I), 5-nitro-1,3-dioxane (III) and 5-nitro-hexahydropyrimidine (IX) derivatives substituted with alkyls in position 5. The nitro group is axial and bulky substituents (R′ = t-C_4H_9, cyclohexyl) in positions 3 of compounds I and IX and also benzyl in position 3 in derivatives of IX are equatorial.

Groups (R′ = CH_3, C_2H_5, n-C_4H_9, $CH_2C_6H_5$) in position 3 of tetrahydro-1,3-oxazine derivatives I are probably axial.

(2) When R is H in 5-nitro-tetrahydro-1,3-oxazine (I), i.e. the secondary nitro group is present, the chair ring can be subjected to rapid conversion and both axial and equatorial conformations of the nitro group are possible.

It seems that equatorial nitro group is present in 5-nitro-hexahydropyrimidine derivatives (IX) when R = H.

(3) The ring of investigated 5-nitro-2-bora-1,3-dioxane derivatives (IV) is of "semi planar" form.

(4) The ring of investigated derivatives of 1,5-diazacyclo-octane (X) has a crown form.

(5) The condensed rings of investigated 1,5-diazabicyclo(3.3.3)undecane derivatives (XI) are of "propeller" form.