467. *The Stereochemistry of Some* 1 : 5-*Diaza*cyclo*octane Derivatives.**

By R. Koliński, (Miss) H. Piotrowska, and T. Urbański.

The dipole moments of *cis*- and *trans*-3 : 7-diethyl-3 : 7-dinitro-1 : 5-diaza*cyclo*octane indicate that the ring is in the " crown " form. 3 : 7-Dialkyl-3 : 7-dinitro-1 : 5-diaza*cyclo*octanes form only monohydrochlorides and mononitroso-derivatives, which is considered to be due to internal hydrogen bonding: this is confirmed by infrared absorption spectra.

3 : 7 : 10-Triethyl-3 : 7 : 10-trinitro-1 : 5-diaza*bicyclo*[3 : 3 : 3]undecane is composed of two fused 1 : 5-diaza*cyclo*octane rings, which are held to a " double-chair " form on the basis of the dipole moment.

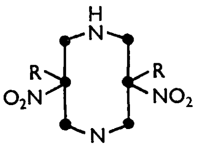
The preparation of 3 : 7-dialkyl-3 : 7-dinitro-1 : 5-diaza*cyclo*octanes from primary nitroparaffins, formaldehyde, and ammonia has been described,[1] nitroethane, 1-nitropropane, and 1-nitrobutane yielding the compounds (I; R = Me, Et, and Pr^n respectively). We now show that the diethyl compound has the *trans*-configuration.

---

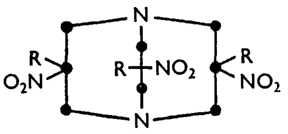
* Communicated at the 16th Congress of Pure and Applied Chemistry, Paris, 1957.

[1] Urbański and Lipska, *Roczniki Chem.*, 1952, **26**, 182; Urbański and Piotrowska, *ibid.*, 1955, **29**, 379; Jones, Koliński, Piotrowska, and Urbański, *ibid.*, 1957, **31**, 101.

1-Nitropropane also furnished the *cis*-isomer (I; R = Et), and a compound with two fused 1 : 5-diaza*cyclo*octane rings, namely, (II; R = Et).[2] On careful hydrolysis the latter gave a mixture of the *cis*- and the *trans*-isomer (I; R = Et). The same mixture was obtained when 2-hydroxymethyl-2-nitrobutan-1-ol was warmed with an excess (5 mol.) of ammonia. The isomers were separated by virtue of the greater solubility of the *cis*-hydrochloride (it is interesting that free *cis*-amine was the *less* soluble isomer).



(I)



(II)

Although chemical proof of the structures (I) and (II) was given earlier,[1, 2] we considered it advisable to check the structures by determining the molecular refractions of the compounds: these proved to be in agreement with calculated figures see Table.

	M_R		NH frequencies (cm.$^{-1}$)				NO$_2$ frequencies (cm.$^{-1}$) *	
				Stretching				
Compound	Expt.	Calc.	Free	Free (?)	Bonded	Deformn.	Free	Bonded
I; R = Me	56·20	56·30	3448	3295	3228	1613w	1361s	1325
cis-I; R = Et	65·83	65·53	3475	3320	3190	1681w	1361	—
trans-I; R = Et ...	65·90	65·53	3475	3320	3228	1653w	1351	1333sh
I; R = Pr^n	74·95	74·76	3475	3320	3220	1653	1361	1333sh
II; R = Et	92·50	92·16	—	—	—	—	—	—

(w = weak, s = strong, sh = shoulder)

* For the region of asymmetric NO$_2$ vibrations (6·5 μ) *cyclo*hexane solutions were used. The thin layer (1 mm.) required a relatively high concentration (0·025 mole l.$^{-1}$). Two frequencies were found 1563—1587 (free NO$_2$) and 1538 cm.$^{-1}$ (bonded NO$_2$). As the dilution was probably insufficient to break intermolecular hydrogen bonds, these figures have not been considered in our discussion.

The diaza*cyclo*octanes (I) form only monohydrochlorides and mononitroso-derivatives, believed[3] to be due to internal hydrogen bonding between the two secondary nitrogen atoms ($\rangle$NH • • • NH$\langle$) or between one of the amino- and one of the nitro-groups. Infra-red absorption spectra have now brought evidence of both free and bonded NH and NO$_2$ groups. The Table shows the maxima for CCl$_4$ solutions and their assignments. Three NH bands have been found in the region of higher frequencies (*ca.* 3475, 3320, and 3200 cm.$^{-1}$). Since internal hydrogen-bonding produces a small fall of frequency (usually less than 100 cm.$^{-1}$),[4] we assign the frequencies 3475 and 3320 cm.$^{-1}$ to free and the frequency 3200 cm.$^{-1}$ to bonded NH groups. For the nitro-groups two frequencies of symmetric vibrations have been noticed: one corresponding to the free nitro-group, the other, lower by 18—36 cm.$^{-1}$, to the bonded nitro-group, in accordance with earlier work.[3] Work on the hydrochlorides and nitroso-derivatives is in progress.

In a study of the stereochemistry various ring forms were by means of molecular models found to be impossible. Finally three ring forms needed consideration: the crown form (*A*) (Fig. 1), the double-chair form (*B*), and the skew form (*C*).

Dipole moments were calculated and measured for derivatives of 1-nitropropane, *i.e.*, the *cis*- and the *trans*-isomer (I; R = Et) and compound (II; R = Et), which were conveniently soluble in benzene. Group moments NH 1·3 D and NO$_2$ 3·5 D, and the

---

[2] Jones, Koliński, Piotrowska, and Urbański, *Bull. Acad. polon. Sci.*, Cl. III, 1956, **4**, 521; *Roczniki Chem.*, 1957, **31**, 101.

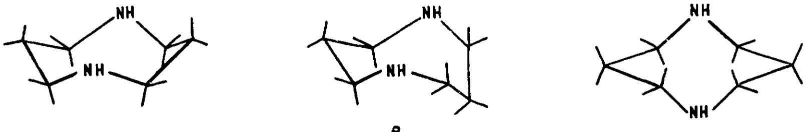
[3] Urbański, *Bull. Acad. polon. Sci.*, Cl. III, 1953, **1**, 239; 1954, **2**, 393; 1956, **4**, 87, 381; 1957, **5**, 533; Urbański and Ciecierska, *Roczniki Chem.*, 1955, **29**, 11; Urbański, *ibid.*, p. 375; 1957, **31**, 37.

[4] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1956, p. 215

CNC angle 110° were assumed in calculations. The experimental value for *trans*-isomer was found to be 5·4 D, which fitted to form (*A*) with two possible conformations of two nitro-groups, namely, axial and equatorial (*i.e., trans*) (μ = 5·4 D) (Fig. 2), and both axial (*i.e., cis*) (μ = 6·0 D) (Fig. 3, where all possible hydrogen bonds are shown on one diagram).

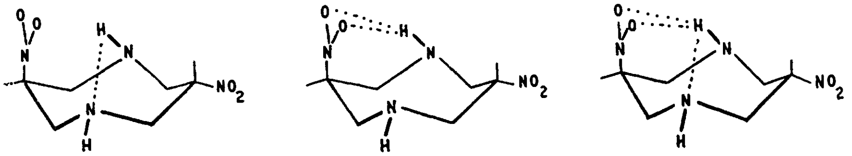
By analogy with *cyclo*hexane derivatives a form with equatorial conformation should be considered more probable, so preference is given to the conformation of Fig. 2.

FIG. 1.



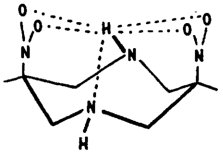
A *B* *C*

FIG. 2.



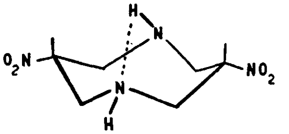
1 *2* *1-2* *A*(*ae*)

FIG. 3.



A(*aa*)

FIG. 4.



A(*ee*)

In either form a NO_2–HN hydrogen bond would be possible, the distance between H and O being *ca.* 2·5 Å. Only one bond of the type $>$NH • • • NH$<$ is possible in form (*A*) (bond length *ca.* 2·0 Å).

If both nitro-groups were equatorial (*i.e., cis*) in form (*A*) (Fig. 4) the calculated value of μ was 4·3 D. This is in agreement with the experimental value (4·6 D) for the *cis*-isomer (I; R = Et).

It is evident that the conformation of Fig. 4 could be obtained from that of Fig. 3 by a simple ring conversion. As equatorial conformations are more likely, the latter is more stable and therefore more probable.

Consequently, we accept conformation ae of Fig. 2 for the *trans*- and conformation ee of Fig. 4 for the *cis*-isomer (I; R = Et).

The two other forms (*B*) and (*C*) of Fig. 1 should be rejected, because the calculated values of the dipole moment were lower than the experimental figures. Thus, for form (*B*) the values for different conformations of nitro- and ethyl groups were 3·0, 3·6, and 3·5 D. For form (*C*) values were calculated to be 1·9, 3·2, 0, and 3·5 D. It has been established by means of models that the bicyclic compound (II; R = Et) can exist in two forms only: both possess B rings and conformation of the nitro-group is either symmetric (Fig. 5) or asymmetric (Fig. 6). Their calculated dipole moments are 0 and 5·5 D respectively. The experimental value was 5·7 D. Thus, the asymmetric structure (Fig. 6) should be accepted.

It should be pointed out that the 1 : 5-diaza*cyclo*octane ring occurs in sparteine and a number of similar alkaloids.[5] Further analogy with sparteine exists in substitution of these rings in the positions 3 and 7.

FIG. 5.

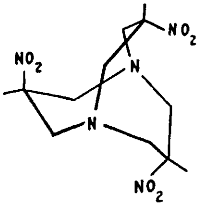
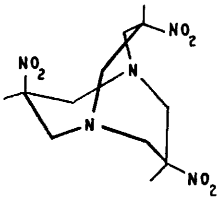


FIG. 6.



EXPERIMENTAL

3 : 7-*Diethyl*-3 : 7-*dinitro*-1 : 5-*diaza*cyclo*octane Hydrochlorides*.—(*a*) 2-Hydroxymethyl-2-nitrobutan-1-ol (15 g., 0·1 mol.) was kept in 25% aqueous ammonia (34 ml., 0·5 mol.) for 1 hr. on a steam-bath. Resin separated and was dissolved in alcoholic hydrogen chloride. A mixture of *cis*- and *trans*-hydrochlorides separated at 0° during 3 days. Fractional crystallisation from alcohol gave the less soluble *trans*-hydrochloride, m. p. 172—173° (decomp.). The more soluble fraction was the cis-*hydrochloride*, m. p. 169—171° (decomp.) (0·07 g., 0·5%) (Found: C, 40·5; H, 7·2; N, 19·1. $C_{10}H_{20}O_4N_4$,HCl requires C, 40·4; H, 7·1; N, 18·8%).

(*b*) The amine (II; R = Et) (2 g.) was heated on a steam-bath with ethanolic hydrogen chloride (15 ml.), then left at 0° overnight. Mixed hydrochlorides (1·3 g.) were precipitated; fractionation as in the method (*a*) gave the *cis*-hydrochloride, m. p. 169—171° (decomp.) (0·15 g., 11%).

cis-3 : 7-*Diethyl*-3 : 7-*dinitro*-1 : 5-*diaza*cyclo*octane*.—The *cis*-base was prepared by neutralisation of an aqueous solution of the *cis*-hydrochloride with sodium hydroxide and extraction with ether; crystallised from ether and then alcohol, it had m. p. 94—95° [Found: C, 46·2; H, 7·7; N, 21·8%; *M* (Rast), 254. $C_{10}H_{20}O_4N_4$ requires C, 46·1; H, 7·7; N, 21·6%; *M*, 260].

cis-N-*Nitroso-derivative*.—The above *cis*-hydrochloride (0·2 g.), dissolved in small amount of water, was acidified with 10% hydrochloric acid, and 20% aqueous sodium nitrite was added. The solid N-*nitroso-compound* was extracted with ether and crystallised from ethanol (yield, 0·1 g.; m. p. 139—140°) (Found: N, 24·4. $C_{10}H_{19}O_5N_5$ requires N, 24·2%). With concentrated hydrochloric acid at 60° it yielded the hydrochloride of the *cis*-isomer (I; R = Et).

Dipole Moments.—These were measured by the heterodyne beat method, with benzene as a solvent. The results were extrapolated by the method of Le Fèvre and Vine.

Infrared Absorption Spectra.—The spectra were measured by means of Hilger single-beam spectrophotometer type H-668, for CCl_4 solutions (0·0025—0·005 mole $l.^{-1}$) in 5 cm. layers. The optics were of sodium chloride: for the range 2·5—3·5 μ optics of lithium fluoride were used.

Molecular Refractions.—These were determined from refractive indexes, measured in benzene, dioxan, or carbon tetrachloride. The results for various solvents were the same within experimental error.

We are much indebted to Professor D. Ginsburg of Haifa Technion for supplying us with atomic models (Catalin Products Ltd.). We thank also Professor W. Tomassi, Dr. H. Calus, and Miss H. Jankowska for measuring the dipole moments, Mr. T. Traczyk for calculating some of the dipole moments, and Dr. (Mrs.) J. Świętosławska, Miss B. Kontnik, and Miss T. Kraczkiewicz for measuring the infrared spectra.

INSTITUTE OF ORGANIC SYNTHESIS, POLISH ACADEMY OF SCIENCES,
WARSAW 10, POLAND.
[*Received, July* 16*th*, 1957.]

---

[5] Clemo, Morgan, and Raper, *J.*, 1936, 1025.