365. *The Stereochemistry of Some Hexahydropyrimidine Derivatives.*

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The conformations of some hexahydro-5-nitropyrimidines were determined by dipole-moment measurements; all are in the chair form with the 5-nitro-group axial and equatorial when alkyl and hydrogen, respectively, are at position 5.

The preparation of derivatives of hexahydro-5-nitropyrimidines from primary nitroparaffins, formaldehyde, and ammonia or primary amines, has been described.[1,2] Hexahydro-5-nitropyrimidines (I) examined were 1,3-dibenzyl- or 1,3-dicyclohexyl-derivatives carrying also a hydrogen, methyl, ethyl, or propyl group at $C_{(5)}$. The dipole moments indicate that the ring is in the chair conformation with the cyclohexyl or benzyl groups equatorial. The conformation of the nitro-group depends on the size of the other substituent at $C_{(5)}$.

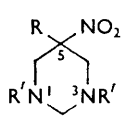
Dipole moments were calculated on the basis of 3·5 D for the moment of the nitro-group, 0·45 D for the C–N bond moment, and 110° for the CNC angle. Experimental values (in D) were:

$R' = CH_2Ph$; R =	Me	Et	Pr^n	$R' = C_6H_{11}$; R =	Me	Et	Pr^n
	4·43	4·36	4·43		4·39	4·45	4·41

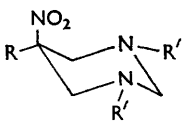
[1] Senkus, *J. Amer. Chem. Soc.*, 1946, **68**, 1611.

[2] Malinowski and Urbański, *Roczniki Chem.*, 1951, **25**, 183; Urbański and Lipska, *ibid.*, 1952, **26**, 182; Urbański, Biernacki, and Lipska, *ibid.*, 1954, **28**, 169; Urbański and Piotrowska, *ibid.*, 1955, **29**, 329.

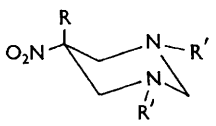
when they are compared with the calculated values shown below the formulæ, closest agreement with (A), in which R′ is equatorial and the nitro-group axial, is apparent.



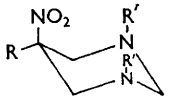
(I)



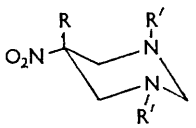
(A, 4·35)



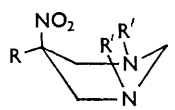
(B, 3·12)



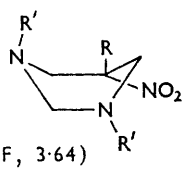
(C, 3·72)



(D, 3·06)



(E, 2·55)



(F, 3·64)

Experimental values for (I; R = H, R′ = CH_2Ph and C_6H_{11}) were **3·15** and **3·18** D, respectively, suggesting that these compounds exist in form (B).

Experimental

1,3-*Dicyclohexylhexahydro-5-methyl-5-nitropyrimidine.*—2-Methyl-2-nitropropane-1,3-diol (13·5 g., 0·1 mol.) (from nitroethane and formaldehyde), 36% aqueous formaldehyde (8·3 ml., 0·1 mol.), cyclohexylamine (19·8 g., 0·2 mol.), and methanol (60 ml.) were refluxed for 8 hr. After cooling and being set aside overnight, the *product* was filtered off. The yield was 26·2 g. (85%), m. p. 78—79° (from ethanol) (Found: C, 66·2; H, 10·1; N, 13·8. $C_{17}H_{31}N_3O_2$ requires C, 66·0; H, 10·0; N, 13·6%).

1,3-*Dicyclohexyl-5-ethylhexahydro-5-nitropyrimidine.*—This was prepared as above from 2-ethyl-2-nitropropane-1,3-diol (14·9 g., 0·1 mol.) (from 1-nitropropane and formaldehyde), formaldehyde (8·3 ml., 0·1 mol.), and cyclohexylamine (19·8 g., 0·2 mol.). The *pyrimidine* (28·1 g., 87%) had m. p. 67—68° (Found: C, 67·0; H, 10·3; N, 13·0. $C_{18}H_{33}N_3O_2$ requires C, 66·8; H, 10·2; N, 13·0%).

1,3-*Dicyclohexylhexahydro-5-nitro-5-propylpyrimidine.*—The compound was prepared as above from 2-nitro-2-propylpropane-1,3-diol (16·3 g., 0·1 mol.) (from 1-nitrobutane and formaldehyde), 36% aqueous formaldehyde (8·3 ml., 0·1 mol.), and cyclohexylamine (19·8 g., 0·2 mol.). The *pyrimidine* (26·9 g., 80%) had m. p. 59—60° (Found: C, 67·6; H, 10·5; N, 12·6. $C_{19}H_{35}N_3O_2$ requires C, 67·5; H, 10·4; N, 12·4%).

1,3-*Dicyclohexylhexahydro-5-nitropyrimidine.*—1,3-Dicyclohexylhexahydro-5-hydroxymethyl-5-nitropyrimidine (1·62 g., 0·005 mol.) in methanol (20 ml.) was mixed with a 2% solution of sodium methoxide in methanol (13·5 ml., 0·005 mol.) and heated for 5 min. at 40—45°. The mixture was cooled and dry ether (200 ml.) was added. The precipitated sodium salt was filtered off, dissolved in water (20 ml.) and carefully neutralized with an aqueous solution of hydroxylamine hydrochloride. It was extracted with ether, the extract was dried and evaporated, and the residue crystallized from ethanol. The *product* (0·44 g., 30%) had m. p. 42—43° (Found: C, 66·1; H, 10·1; N, 14·3. $C_{16}H_{29}N_3O_2$ requires C, 66·0; H, 9·9; N, 14·2%).

1,3-*Dibenzylhexahydro-5-nitropyrimidine.*—The compound was prepared as above from 1,3-dibenzylhexahydro-5-hydroxymethyl-5-nitropyrimidine (1·7 g., 0·005 mol.) and 2% sodium methoxide in methanol (13·5 ml., 0·005 mol.). The *pyrimidine* (0·54 g., 35%) had m. p. 57—58° (Found: C, 69·1; H, 6·8; N, 13·6. $C_{18}H_{21}N_3O_2$ requires C, 68·9; H, 6·7; N, 13·5%).

Dipole-moment Measurements.—These were made by the heterodyne-beat method on a DMI instrument (Wissenschaftliche Technische Werkstätte, Weilheim).

We thank the van't Hoff Foundation, Royal Academy of Science of the Netherlands, for Dreiding Stereomodels.

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[*Received, August* 23*rd*, 1961.]