

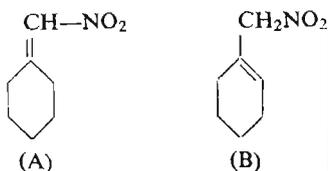
On Endo- and Exoisomers of Nitroolefins (1-Cyclohexenyl- and Cyclohexylidenenitromethane). III. Dipole Moments Measurements

by

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In the course of our studies of the olefinization reaction of 1-nitromethyl-1-hydroxycyclohexane acetyl derivative we found previously [1] that, depending on the conditions under which the above reaction was run, 1-cyclohexenyl nitromethane (B) or the mixture (A)+(B) of cyclic nitroolefins is formed:



Analysis of the infrared absorption spectra allowed to determine the quantitative proportion of exo- (A) and endoisomers (B) in the mixture [2].

In order to obtain further evidence confirming the presence of the exo form of nitroolefin, which is generally considered not very probable [3], the dipole moments determination method was applied.

The presence of the double bond in the neighbourhood of the carbon with a nitromethylidene substituent indicated the existence of conjugation of π , σ -type with the nitrogroup in the case of the exoisomer. Therefore an increase of dipole moment value as compared to the dipole moment of the separate nitrogroup in the endoisomer molecule was to be expected.

The above argumentation found confirmation in the fact described in literature for the compounds with a β -nitrovinyl substituent [5]—[7]. The dipole moment of the β -nitrovinylbenzene molecule is larger by *c.* 1 *D* as compared with that of unsaturated compounds with separate nitrogroup, amounting to 4.5 *D*. The conjugation effect changes depending on the kind of substituent at *para*-position of the benzene ring [7].

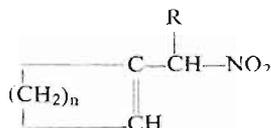
For the determination of the dipole moments of the mixture consisting of nitroolefins (A) and (B), the value of the dipole moment of the endoisomer was

unknown. It should be assumed that it will not differ, because of the isolation of the double bond, from the dipole moment of the nitrogroup.

Taking into consideration the lack of data on dipole moments values for cyclic nitroolefins of this type, the dipole moments for the homologous series of cyclohexenyl- (I), cycloheptenyl- (II), cyclooctenylnitromethane (III) and for the unsaturated cyclohexane derivatives with alkyl substituent attached to carbon with the nitrogroup (IV), (V), or to the alicyclic system (VI) have been determined.

For comparison we have also determined the dipole moments of nitromethyl- (VII) and nitrocyclohexane (VIII). Preparation of nitrocyclohexane of high purity, was achieved by acting on 1-nitro-1-hydroxymethylcyclohexane with potassium hydroxide in presence of nitromethane.

TABLE I
Dipole moments of nitroolefins of general formula:



No.	R	n	P_∞	MR_n	$\mu (D)$	Method of preparation
(I)	H	4	311	37.71	3.6	[1], [2]
(II)	H	5	326	42.25	3.6	[8]
(III)	H	6	321	46.76	3.6	[9]
(IV)	CH ₃	4	315	42.25	3.6	[13]
(V)	C ₂ H ₅	4	324	46.75	3.6	[13]

TABLE II
Dipole moments of other nitroparaffins

No.	Formula	P_∞	MR_D	$\mu (D)$	Method of preparation
(VI)	CH ₃  CH ₂ NO ₂	308	42.05	3.5	[10]
(VII)	 CH ₂ NO ₂	294	38.18	3.5	—
(VIII)	 NO ₂	314	33.39	3.6	—

The data of dipole moments values are tabulated (Tables I and II). The determined dipole moments data are very near to the value of 3.6 *D* (experimental error $\pm 0.1 D$). This indicates that the cyclic system, especially with the separate double bond, does not influence the dipole moment of the molecule. This is due exclusively to the presence of the aliphatic nitrogroup.

The results of measurements of dipole moments of the nitroölefins mixture consisting of endo- and exoisomers (IX) obtained after dehydroacetylation of 1-nitromethylcyclohexanol-1 acetic ester [1] are tabulated (Table III).

The dipole moment was found to be 4.3 D. It is higher by *c.* 0.7 D than that determined for the other cyclic nitroölefins with separated double bond or for saturated cyclonitroparaffins (Tables I—II). This fact could be explained by the conjugation between the double bond and the nitrogroup in the nitroölefin molecule. It confirmed the existence of the exoisomer in the mixture of nitroölefins.

TABLE III

Dipole moments of primary mixture of exo- and endoisomers (A) + (B) and of artificially prepared mixtures after addition of 1-cyclohexenylnitromethane (B)

No.	Per cent of added endoisomer (B)	P_{∞}	MR_D	μ (D)
(IX)	0	436	39.09	4.3
(X)	20.84	433	38.79	4.3
(XI)	44.57	413	38.47	4.2
(XII)	47.77	375	38.20	4.0

The high value of the above dipole moment indicates the high amount of cyclohexylenenitromethane (A) in the mixture. After diluting the mixture of nitroölefins by addition of 1-cyclohexenylnitromethane (B) (prepared according to [11]) we tried to evaluate qualitatively the proportion of both isomers in the primary mixture by measuring dipole moments of the diluted mixture.

The results summarized in Table III seem to support the view of the definite quantitative predominance of the exoisomer. After addition of about 50 per cent of the endoisomer the determined dipole moment (XII) diminished to the value of 4.0 D. On the other hand, *c.* 60 per cent increase of the dipole moment was noted in comparison to that of 1-cyclohexenylnitromethane. Consequently, we may assume that the amount of the endoisomer in the primary mixture was *c.* 10 per cent. This is in agreement with our former conclusion based on the IR-absorption spectra analysis [2].

Experimental

The dipole moments were determined by the dielectric constant measurements by the heterodyne-beat method (0.7 Mc) with condenser (M.W. Sullivan — London) of 1200 pF capacity in anhydrous benzene solution. The density was measured with an Ostwald-type pycnometer of 9 cm³. The results were extrapolated by the method of Le Fevre and Vinc [12]. The dipole moments were calculated from the formula:

$$\mu = 0.01273 \sqrt{(P_{\infty} - P_E) T},$$

where μ —dipole moment value in Debye units, P_{∞} —molar polarization extrapolated to infinite dilution, P_E —electronic polarization equal to molar refraction (MR_D), T —absolute temperature. The ex-

perimental error was $\pm 0.1 D$. The dielectric constants and densities of the mixtures were measured at 20°C in benzene. Benzene was of high purity. Its physical constants were as follows: d_{20}^{20} 0.8788, n_D^{20} 1.5061 and ϵ_{20} 2.2832.

Cyclohexylnitromethane (VII) was prepared by the V. Meyer reaction from cyclohexylmethyl iodide. The resulting mixture of nitroparaffin and nitrous acid ester was subjected to alkaline hydrolysis with sodium hydroxide in aqueous solution to remove the ester. Cyclohexylmethyl iodide was obtained from cyclohexylmethyl bromide, which in turn was prepared by the Hunsdiecker reaction from cyclohexylacetic acid.

Cyclohexylmethyl bromide

The solution of 26 ml. of bromine in 80 ml. of carbon tetrachloride was added, under stirring, to the suspension of 124 g. (0.5 mole) of dried and powdered silver salt of cyclohexylacetic acid in 600 ml of anhydrous carbon tetrachloride. After the exothermic reaction had subsided the mixture was refluxed for 30 min. Silver bromide was filtered off and after removing the excess of the solvent, the residue was distilled under reduced pressure to produce 40 g. (45% of theoretical yield) of cyclohexylmethyl bromide, b.p. $76^{\circ}\text{C}/10$ mm. Hg, n_D^{22} 1.4912.

Cyclohexylmethyl iodide

The solution of 38 g. 0.2 mole of cyclohexylmethyl bromide and 44 g. (0.25 mole) of dried sodium iodide in 250 ml. of anhydrous acetone was refluxed for 3 hours. The separated sodium bromide was filtered off and refluxing was continued for 12 hours. After evaporation of the solvent the residue was distilled under reduced pressure to produce 31 g. (69% of theoretical yield) of cyclohexylmethyl iodide b.p. $69^{\circ}\text{C}/1$ mm.Hg.

Cyclohexylnitromethane (VII)

To the suspension of 28 g. silver nitrite in 100 ml. of carbon tetrachloride 31 g. of cyclohexylmethyl iodide was added dropwise and the mixture was refluxed under stirring for 3 hours. The separated silver iodide was filtered off and washed with a small quantity of carbon tetrachloride. After evaporation of solvent the residue was distilled under reduced pressure to yield 18 g. of the product, b.p. $66\text{--}68^{\circ}\text{C}/2$ mm Hg. This consisted of the mixture of cyclohexenylnitromethane and cyclohexylmethyl nitrite. In order to isolate the pure nitroparaffin from the mixture, it was dissolved in the solution of 4.2 g. of sodium hydroxide and 0.25 ml. of diethylamine in 120 ml. water. After stirring for 45 min. at 22°C the resulting mixture was extracted with ether. The solution of 7 g. of hydroxylamine hydrochloride in 20 ml water was then added, with vigorous stirring, to the aqueous layer. After stirring at room temperature for 1 hour the separated nitroparaffin was extracted with ether. The organic layer was washed with water to neutral reaction and dried over anhydrous sodium sulphate to remove traces of water. Evaporation of solvent gave the residue which was distilled under reduced pressure. Cyclohexylnitromethane was collected at $80^{\circ}\text{C}/4$ mm Hg. The yield was 4 g., n_D^{20} 1.4638, d_{20}^{20} 1.0343, MR_D (calc.) 38.21; MR_D (found) 38.18.

Cyclohexylnitromethane thus obtained did not show in the infrared absorption spectrum the band characteristic for the nitrous ester.

Nitrocyclohexane (VIII)

The solution of 23 g. potassium hydroxide was added dropwise under stirring, to the suspension of 24 g. (0.16 mole) of 1-nitro-1-hydroxymethylcyclohexane in 110 ml. water. The latter was prepared according to [14]. The temperature rose from 18° to 29°C and the solution became clear. Subsequently 4.7 g. of nitromethane was added. The temperature rose to 34°C . The stirring was continued for 25 min. After external cooling with ice and salt mixture, 25 ml. of acetic acid was added dropwise during 15 min. at such a rate as would not raise the temperature above 0°C . The

mixture was stirred for a further 30 min. and extracted with ether by a continuous method during 1.5 hour. The ether solution was dried over anhydrous magnesium sulphate and evaporated. The remaining product was distilled under reduced pressure. Nitrocyclohexane was collected at 84°C/10 mm Hg. Yield 16 g. (80% of theory), d_{20}^{20} 1.0628, n_D^{20} 1.4618, MR_D (calc.) 33.56; MR_D (found) 33.39.

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