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NMR CONFORMATIONAL STUDY OF CYCLIC PRODUCTS FROM DEGRADATION OF HEXAMETHYLENETETRAMINE. HEXAHYDRO-1,3,5-TRIAZINES AND OCTAHYDRO-1-3-5-7-TETRAZOCINES

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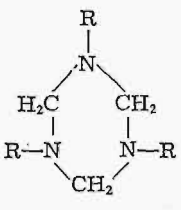
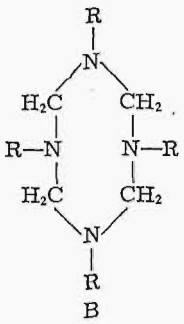
Na podstawie badań NMR stwierdzono, że pochodne heksahydro-1, 3, 5--triazyny charakteryzują się szybką inwersją konformacji krzesłowej z jednoczesną izomeryzacją na atomach azotu. W przypadku 1-3-5-trójnitrozoheksahydro-1, 3, 5-triazyny zaobserwowano zahamowaną rotację dookoła wiązań N—N. Oktahydro-1,3,5,7-tetrazocyny ulegają także szybkiej inwersji pierścienia (prawdopodobnie form koronowych) i izomeryzacji (zmianie konfiguracji) na atomach azotu.

При помощи ЯМР установлено, что производные гексагидро-1,3,5-триазина характеризуются быстрой инверсией кресловидной конформации с одновременной изомеризацией на атомах азота. В случае 1,3,5-тринитрозогексагидро-1,3,5-триазина замечено кроме того заторможенное вращение вокруг связи N—N. Октагидро-1,3,5,7-тетразоцины тоже подвергаются быстрой инверсии кольца (по всей вероятности коронной формы) и изомеризации (перемене конфигурации) на атомах азота.

The NMR analysis of a number of hexahydro-1,3,5-triazine derivatives indicates that the chair form is subject to rapid change in the conformation, and to simultaneous isomerization at the nitrogen atoms. In the instance of 1, 3, 5-trinitrosohexahydro-1, 3, 5-triazine restricted rotation round the N—N bonds is detected in addition to the ring inversion. Octahydro-1,3,5,7-tetrazocines are also subject to rapid ring inversion (probably in the crown form) and to isomerization i.e. change of configuration at the nitrogen atoms.

There are three groups of cyclic products of degradation of hexamethylenetetramine. They are derivatives of hexahydro-1, 3, 5,-triazine (A), octahydro-1, 3, 5, 7-tetrazocine (B), and 1, 3, 5, 7-tetraazabicyclo-[3.3.1]--nonane (C) formed by the consecutive degradation of the original hexamethylenetetramine skeleton [1]. The degradation of hexamethylenetetramine by removing three methylene and one amino group yields hexahydro-1, 3, 5-triazine derivatives (I—XVII); by removing two methylene groups-octahydro-1, 3, 5, 7-tetrazocine derivatives (XVIII—XX); by removing one methylene group-1, 3, 5, 5-tetraazabicyclo-[3.3.1]-nonane derivatives (the latter group of compounds will be discussed in our next paper).


A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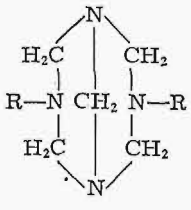
C

The purpose of this work has been to elucidate the problem of conformation of these compounds using nuclear magnetic resonance as a convenient tool.

The starting substance, hexamethylenetetramine, shows only a singlet in the NMR spectrum, as should be expected from the fact that all protons of methylene groups are situated identically and symmetrically to the rest of the molecule. All protons are equivalent from the point of view of NMR. The chemical shift is $\tau = 5.28$ ppm.

EXPERIMENTAL

The following 1, 3, 5-trisubstituted hexahydro-1, 3, 5-triazines and 1, 3, 5, 7-tetrasubstituted octahydro-1, 3, 5, 7-tetrazocines were examined: trimethyl (I), triethyl (II), tri-*n*-propyl (III), tricyclohexyl (IV), tribenzyl (V), tri-(*p*-methylbenzyl)

Table 1

Properties of examined compounds

No	Compound	Boiling(*) or melting point °C	Literature
1	I	49/10 mm Hg*	5
2	II	82/10 mm Hg*	5
3	III	122/10 mm Hg*	5
4	IV	72.5—73.5	6
5	V	49—50	6
6	VI	134—135.5	6
7	VII	72.5—73.5	6
8	VIII	86—87	6
9	IX	73—74.5	6
10	X	138—140	7
11	XI	129—130	8
12	XII	141—142	9
13	XIII	128—129	9
14	XIV	96—98	10
15	XV	220—222	10
16	XVI	106—107	11
17	XVII	203—204	12
18	XVIII	282—282.5	12
19	XIX	274—275	7
20	XX	308.5—310	7

(VI), tri-(*p*-fluorobenzyl) (VII), tri-(*p*-chlorobenzyl) (VIII), tri-(*o*-chlorobenzyl) (IX), triallyl (X), tricyanomethyl (XI), triphenyl (XII), tri-(*p*-methylphenyl) (XIII), triacetyl (XIV), tribenzoyl (XV), trinitroso (XVI), trinitro (XVII), tetranitro (XVII), tetrabenzoil (XIX), and sym. diacetyldibenzoil (XX). All compounds were prepared according to the literature (Table 1).

The NMR spectra were measured at 60 Mc/sec with a Varian V-4300 C spectrometer. The temperature was 26±0.3°C. Samples were prepared as dilute solutions (about 5% v/v) in carbon tetrachloride, deuteriochloroform, deuterioacetonitrile or deuterioacetone. The spectra were calibrated by the usual side band technique, using tetramethylsilane as the internal reference, with an error of ±0.5 cps. The chemical shifts are reported in τ values. The intensities were measured with a V-3521 integrator.

DISCUSSION

Most of NMR spectra (except compound XVI) show singlets for the ring protons. The singlets do not undergo any appreciable change within the −60 to +150°C range. The lack of any internal chemical shift within a methylene group indicates that its two protons are equivalent, at least statistically.

This is possible under condition that a rapid change in conformation occurs along with simultaneous isomerization of configuration at the nitrogen atoms. This can be represented by Fig. 1.

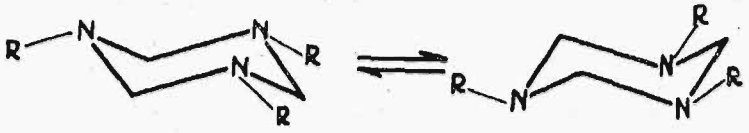

Fig. 1. Inversion of both the hexahydro-1,3,5-triazine ring and the configuration at the nitrogen atoms

Should the change of the conformation occur without any isomerization, the inversion of the ring would bring the axial substituents to the equatorial positions and vice versa, thus leaving the methylene protons still unequivalent. The process may occur either directly, as shown in Fig. 1, with simultaneous inversion of both the ring and the configuration at the nitrogen atoms, or it may involve some intermediate stages, if the inversions are independent of each other. The only requirement is that all species have average lifetimes short enough in comparison with the reciprocal axial-equatorial chemical shift.

The most interesting example of hexahydro-1,3,5-triazines is the 1,3,5--trinitroso derivative. Its NMR spectrum in deuterioacetonitrile at room temperature reveals a symmetrical pattern of three singlets with relative intensities 1:1.66:1 (Fig. 2).

The spectrum implies equivalence of the protons within each methylene group, but nonequivalence of the methylene groups themselves. The equivalence within a methylene group indicates that the ring is statistically planar, from the point of view of NMR. It means that the ring undergoes a rapid inversion of conformation coupled with a rapid inversion of the bonds at the nitrogen atoms; the latter process leaves the substituents in the equatorial positions in all rotamers. If this were not the case, the protons within the methylene group would not be equivalent.

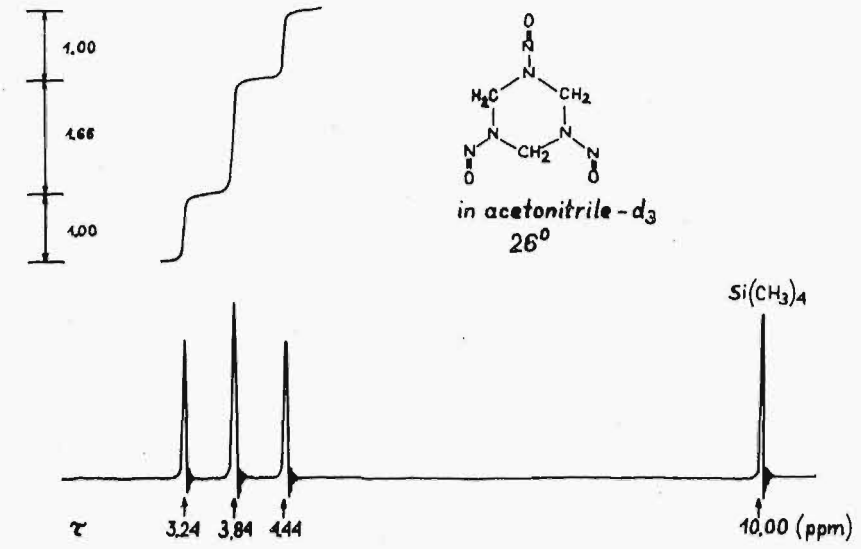

Fig. 2. The NMR spectrum of 1,3,5-trinitrosohexahydro-1,3,5-triazine

The only reasonable explanation of the nonequivalence of the methylene groups is a hindered rotation of the nitroso groups about the N—N bonds [2].

If there is any appreciable delocalization of the lone electron pair from the ring nitrogen atom towards the nitroso group, two semiplanar conformations of the N-nitroso system should be favoured energetically. The

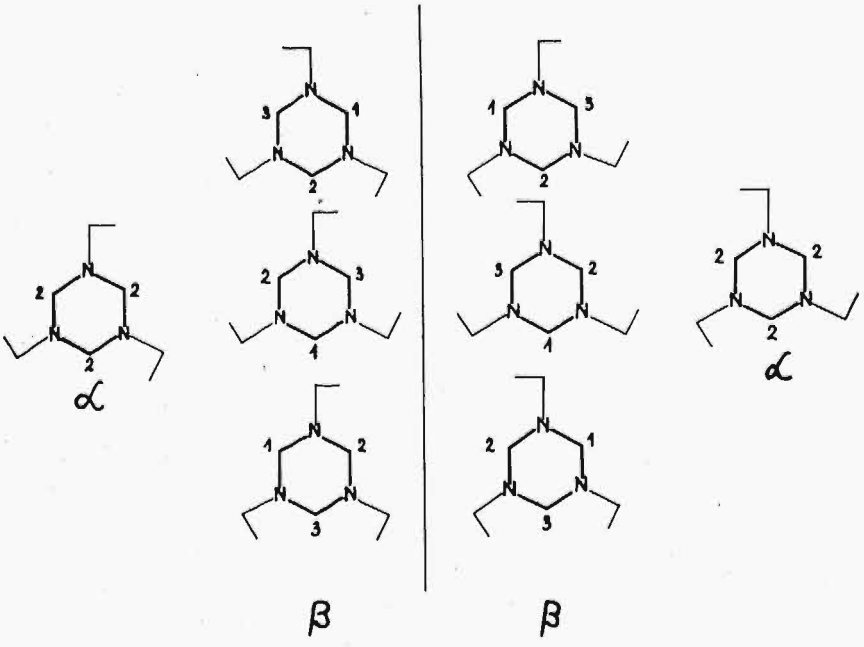

Fig. 3. Statistical distribution of nitroso groups

relative position of the nitroso groups in the trinitroso derivative may be different, thus rendering the methylene groups situated between them magnetically nonequivalent. All possible isomers are shown in Fig. 3.

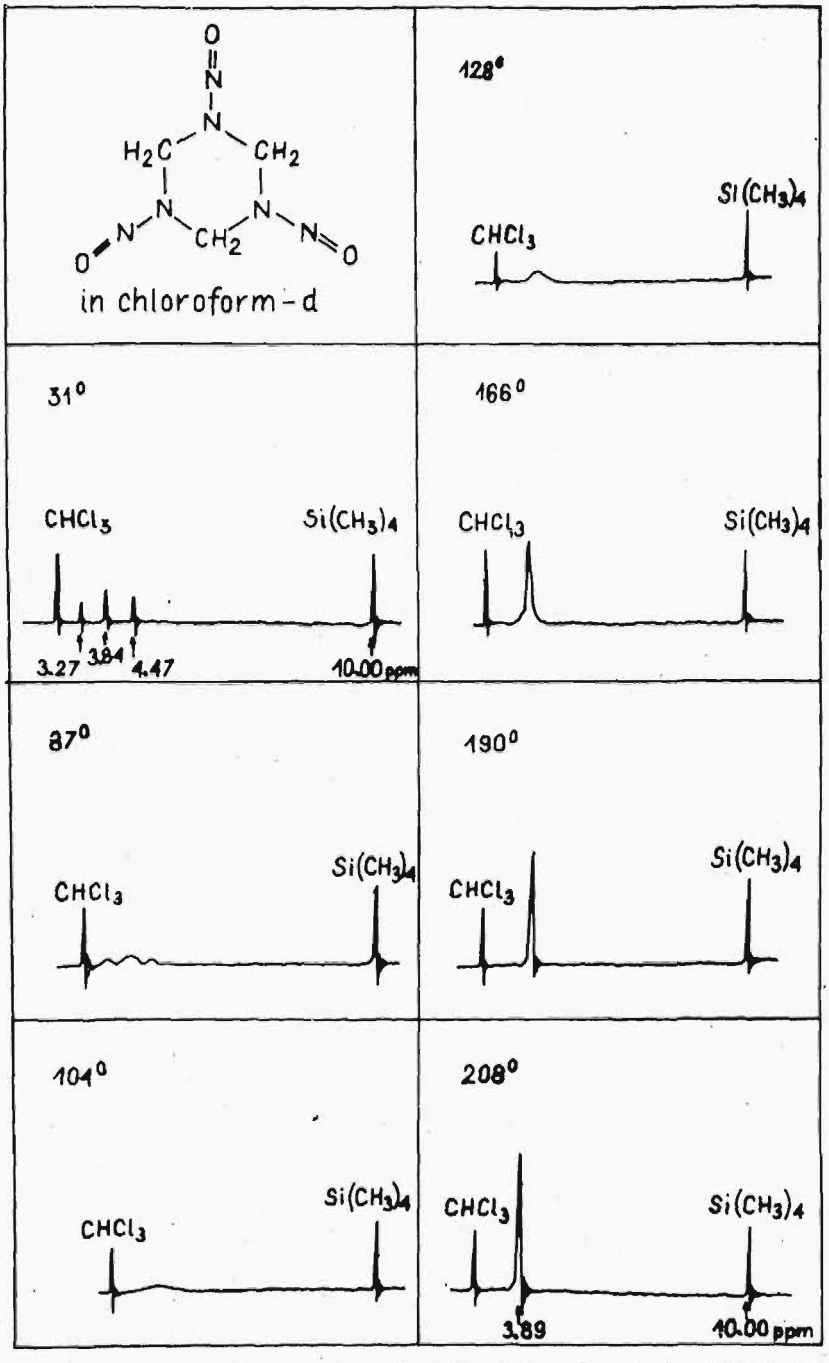

Fig. 4. Temperature investigation of 1,3,5-trinitrosohexahydro-1,3,5--triazine

There are three kinds of methylene groups as far as the orientation of the neighbouring nitroso groups is concerned: one — marked 1, where both the nitroso groups are oriented „out"; another — marked 2, where one of the groups is „in" and the other is „out"; and still another — marked 3, where both the groups are „in". The combination of these arrangements gives two isomers α and β (Fig. 3). If the isomers were energetically equivalent, the intensities of the apparent triplet in the spectrum would be 1 to 2 to 1. The observed ratio of 1:1.66:1 indicates that the β isomer is favoured and there is only 18 per cent of isomer α instead of 25 per cent calculated from the statistical distribution.

On raising the temperature, one should expect an increase in the rate of rotation of the nitroso groups which should lead, eventually, to the complete averaging of all the signals in the spectrum. The measurements carried out at elevated temperatures have borne out that supposition

Fig. 5. Inversion of both the octahydro-1,3,5,7-tetrazocine ring and the configuration at the nitrogen atoms

(Fig. 4). The three singlets broaden and then coalesce at 104°C. After that only one signal is observed; the process of its narrowing practically ends by 208°C.

From the expressions derived by G u t o w s k y [3], it was possible to calculate approximate rates of rotation in the range (Table 2) and draw an Arrhenius plot yielding the activation energy of 22±2 kcal/mole. B l e a r s [4] obtained 25±5 kcal/mole as the activation energy for dimethylnitrosoamine.

The data for a number of derivatives of hexahydro-1,3,5-triazine and octahydro-1,3,5,7-tetrazocine are collected in Tables 3 and 4, respectively.

Table 2

Temperature investigation of 1,3,5-trinitrosohexahydro-1,3,5-triazine (XVI)

No	Temp. t °C	Temp. T °K	$\frac{1}{T}10^{-3}$	Half-width ν in c.p.s.	Life-time τ_i in sec.	$k=\frac{1}{\tau_i}$	$\log k$
1	31	304	3.289	—	—	—	—
2	104	377	2.653	—	0.062	16.1	1.21
3	128	401	2.494	18	0.035	28.6	1.46
4	166	439	2.278	7	0.0085	118	2.07
5	190	463	2.160	3.8	0.00073	1375	3.14
6	208	481	2.079	3.5	—	—	—

With regard to the derivatives of octahydro-1,3,5,7-tetrazocine, they also undergo a rapid inversion of conformation with the change of configuration at the nitrogen atoms down to −60°C.

If the crown form is accepted as energetically most probable, we should postulate the equilibrium shown in Fig. 5.

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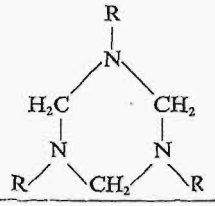
Table 3

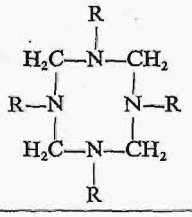
Chemical shifts of hexahydro-1,3,5-triazines (A) (ring protons only)



No	R	τ(p.p.m.)
I	$-CH_3$	6.97
II	$-CH_2CH_3$	6.89
III	$-CH_2CH_2CH_3$	6.86
IV	$-C_6H_{11}$	6.58
V	$-CH_2C_6H_5$	6.70
VI	$-CH_2C_6H_4$-*p*-CH_3	6.74
VII	$-CH_2C_6H_4$-*p*-F	6.64
VIII	$-CH_2C_6H_4$-*p*Cl	6.71
IX	$-CH_2C_6H_4$-*o*-Cl	6.53
X	$-CH_2CH=CH_2$	6.77
XI	$-CH_2CN$	6.38
XII	$-C_6H_5$	5.23
XIII	$-C_6H_4$-*p*-CH_3	5.33
XIV	$-COCH_3$	4.88
XV	$-COC_6H_5$	4.50
XVI	—NO	3.84
XVII	$-NO_2$	3.62

Table 4

Chemical shifts of octahydro-1,3,5,7-tetrazocines (B) (ring protons only)



No_2	R	τ(p.p.m.)
XVIII	$-NO_2$	3.62
XIX	$-C(=O)-C_6H_5$	4.77
XX	1,5 $-C(=O)-CH_3$ 3,7 $-C(=O)-C_6H_5$	4.80

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BADANIA KONFORMACYJNE CYKLICZNYCH PRODUKTÓW DEGRADACJI HEKSAMINY METODAMI NMR. HEKSAHYDRO-1,3,5-TRIAZYNY I OKTAHYDRO-1,3,5,7-TETRAZOCYNY

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Omówiono wyniki badań, metodą protonowego rezonansu magnetycznego, dwóch grup produktów degradacji heksaminy, a mianowicie pochodnych heksahydro-1,3,5-triazyny (I—XVII) i oktahydro-1,3,5,7-tetrazocyny (XVIII—XX). Wszystkie badane związki ulegają w temp. pokojowej szybkiej inwersji pierścienia z równoczesną izomeryzacją konfiguracji na atomach azotu. W przypadku 1,3,5-trójnitrozoheksahydro-1,3,5-triazyny zaobserwowano dodatkowo w temp. pokojowej zahamowaną rotację dookoła wiązań N—N. Widmo NMR składa się tu z trzech singletów o wzajemnej intensywności 1:1,66:1. Świadczy to o równocenności protonów danej grupy metylenowej i nierównocenności samych grup metylenowych. Nierównocenność grup metylenowych wyjaśnić można zahamowaną rotacją atomów wokół wiązań N—N, dzięki której mamy do czynienia z trzema możliwymi usytuowaniami dwóch grup nitrozowych w najbliższym sąsiedztwie danej grupy metylenowej. Dowodem słuszności takiej interpretacji widm NMR trójnitrozowej pochodnej heksahydrotriazyny są badania temperaturowe jego zależności, przejawiającej się w stopniowym uśrednianiu się trzech sygnałów w miarę wzrostu temperatury. Począwszy od 208° obserwuje się już jeden tylko sygnał rezonansowy. Obliczono barierę rotacyjną dla grup nitrozowych, wynoszącą 22±2 kcal/mol.