ASYMMETRIC UNBRIDGED NITROGEN.

39.* CONFIGURATION AND CONFORMATIONS OF N-SUBSTITUTED PERHYDRO-1,3,2-DIOXAZINES

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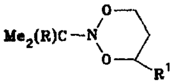
The stereochemical peculiarities of N-substituted perhydro-1,3,2-dioxazines were analyzed thoroughly on the basis of NMR spectroscopic data, the results of x-ray diffraction analysis, and quantitative MO theory. It is shown that in solutions and in the crystalline state these compounds exist in a "chair" conformation with an equatorial orientation of the substituents in the 2 and 4 positions; the high degree of crimped character of the heteroring (the angle of inflection along the O...O line is 70.3°) is due to repulsion of the unshared electron pairs of the N and O atoms and n–σ* interactions. An increase in the n–σ* interaction in dialkoxy amines and acetals on passing from C_s to C_2 symmetry of the molecules was demonstrated.

The first representatives of a new class of heterocyclic compounds, viz., perhydro-1,3,2-dioxazines, were recently synthesized [3]. Continuing our investigation of the stereochemistry of nitrogen-containing heterocycles and the effect of orbital interactions on their structures and physicochemical properties [4-7] we studied the structures of perhydro-1,3,2-dioxazines I-IV by NMR spectroscopy in solution and of amide I by x-ray diffraction analysis in the crystalline state.



I R=MeNHCOCH$_2$; II R=MeO$_2$CCH$_2$; III, IV R=MeO$_2$C; I—III R^1=H; IV R^1=Me

First and foremost, the question of the configurational stability of the N atom in these heterocycles arises. On the basis of the known data it might have been assumed that it is rather high. Thus on passing from acylic monoalkoxy amines to five- and six-membered heterocycles with an N–O fragment the barrier to inversion of the atom increases ≈4 kcal/mole [4, 8, 9]; it increases to an even greater extent on passing from acyclic dialkoxy amines [10] to N-alkoxy-1,2-oxazolidines [11]. In the case of 1,3,2-dioxazolidines (five-membered analogs of perhydro-1,3,2-dioxazines) inversion of the N atom is not observed upon heating to 170° ($\Delta\gamma$ = 2.5 Hz for the ring protons in solutions in nitrobenzene [3]). We have shown that, similar to this, the PMR spectra of II and III in diphenyl ether (80 MHz) do not change even in the case of heating to 190°C, i.e., in six-membered heterocycles with an ONO fragment, just as in five-membered heterocycles [3], the configurational stability of the N atom is higher than in acyclic dialkoxy amines [10] and lies outside the limits of the possibility of measurement by NMR spectroscopy ($\Delta G^{\neq}$ > 27 kcal/mole).

To determine the conformations of the I-IV molecules in solution we studied their ^{1}H and ^{13}C NMR spectra (Tables 1 and 2). The chemical shifts and spin–spin coupling constants (SSCC) of the ring protons were obtained by calculation of the theoretical spectra with a computer; in the case of IV the calculation was made under conditions of decoupling of the protons of

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*See [1] for communication 38. Communication 39 is also communication 25 of the series "Geminal systems." See [2] for communication 24.

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TABLE 1. Parameters of the PMR Spectra of Perhydro-1,3,2-dioxazines I-IV (360 MHz, C_6D_6)

Compound	Chemical shift, δ, ppm						SSCC, J, Hz					
	Me_2C	R	4a-H (6a-H)	4e-H (6e-H)	5a-H	5e-H	4a,4e (6a,6e)	4a,5a (6a,5a)	4a,5e (6e,5a)	4e,5a (6e,5e)	4e,5e (6e,5e)	5a,5e
I	1,4	2,4 (CH_2CO); 2,5 (MeN)[a], 5,1 (HN)[a]	4,0	3,7	1,6	0,6	−12,3	12,3	2,7	5,5	1,1	−13,3
II	1,5	2,7 (CH_2CO)	4,1	3,7	1,7	0,6	−12,2	12,2	2,8	5,4	1,2	−13,4
III	1,6[b]	3,4 (MeO)	4,2	3,8	1,7	0,6	−12,2	12,2	2,7	5,4	1,2	−13,4
IV	1,6[b]	3,4 (MeO)	4,2 (4,1)	0,9[c] (3,8)	1,3	0,8	6,5[d] (−11,1)	11,7 (12,5)	2,6 (2,7)	— (5,2)	— (1,1)	−13,4

[a] $^3J_{HNCH}$ = 4.9 Hz. [b] Two singlets with $\Delta\nu$ = 1.8 Hz. [c] δ_{Me}. [d] $^3J_{4a\text{-}HCCH_3}$.

the methyl group attached to the $C_{(4)}$ atom (Fig. 1). The vicinal SSCC of the protons attached to the $C_{(4)}$ and $C_{(5)}$ atoms of IV constitute unambiguous evidence for an equatorial orientation of the methyl group attached to the $C_{(4)}$ atom. It should be noted that an identical α effect of the equatorial methyl group in IV (Table 2) and in 4-methyl-1,3-dioxane [12] is observed from the ^{13}C spectra. Nonequivalence of the diastereotopic methyl groups of the Me_2CN fragment is manifested in the spectra of chiral compound IV: $\Delta\nu$ = 1.8 Hz (^1H) and 46.3 Hz (^{13}C).

The similarity of the parameters of the NMR spectra of I-IV (Tables 1 and 2) indicates their identical conformation in solution. It might be assumed that they all have a "chair" conformation, since, with respect to the indicated parameters, they are similar to hydrocarbon and phosphorus analogs that have this conformation, viz., 1,3-dioxanes and 1,3,2-dioxo(or dithia)phosphorinanes (see [12-15] and the literature cited in [16, 17]). In analogy with 2-tert-butyl-1,3,2-dioxa(and dithia)phosphorinanes [14] one might also assume an equatorial orientation of the N-tert-alkyl substituent in perhydro-1,3,2-dioxazines. In fact, it was established by x-ray diffraction analysis of I (Tables 3-5[†]) that in the solid phase the perhydro-1,3,2-dioxazine ring has a "chair" conformation with an equatorial orientation of the substituent attached to the N atom (Fig. 2). Retention of this conformation in solution is confirmed by the satisfactory agreement between the experimental values of dihedral angles θ (Fig. 3) and the angles calculated from the SSCC from the equation $^3J_{H,H} = 12.95\cos^2\theta$ [18]. Found (calculated): $H_eCC_{(3)}H_e$ 71.5° and 75.4° (73.1°); $H_eCC_{(3)}H_a$ 45.9° and 47.8° (49.3°); $H_aCC_{(3)}H_e$ 54.9° and 56.1° (62.3°), where C is a $C_{(1)}$ or $C_{(2)}$ atom. The possibility of an axial orientation of the N-tert-alkyl substituent for perhydrodioxazines in solution is evidently excluded, since in I the lengths of the N—O and C—O bonds are shorter than the lengths of the C—C bonds (Table 4), and the angle of inflection of the ring along the $O_{(1)}...O_{(2)}$ axis (70.3°) is considerably greater than in cyclohexane (49.7°, calculated from the data in [19]). The steric interactions between the axial N-tert-alkyl substituent and the hydrogen atoms attached to the $C_{(1)}$ and $C_{(2)}$ atoms should therefore be considerably stronger than in cyclohexanes, for which the conformational energy of the tert-butyl group is already rather high (>4 kcal/mole).

On examining the results of x-ray diffraction analysis of I one must first of all direct one's attention to the significant increase in torsion angle θ (CONO) (76.2°, Fig. 3) as compared with angle (COCO) in 1,3-dioxanes (60-64° [16, 17]) and angle (CCCC) in cyclohexane (54.5° [19]). This can be explained by interactions with the participation of the unshared electron pairs (UEP) and the antibonding orbitals in the heterocycles (Fig. 4): in perhydro-1,3,2-dioxazine by repulsion of the UEP of the N and O atoms and by the $n_pO_{(1)}-\sigma^*[N-O_{(2)}]$ and $n_pO_{(1)}-\sigma^*$ stabilizing interactions; in 1,3-dioxanes by the $n_pO_{(1)}-\sigma^*[C-O_{(2)}]$ and $n_pO_{(2)}-\sigma^*[C-O_{(1)}]$ stabilizing interactions.[‡] In fact it is apparent from the O → N projection (Fig. 3) that dihedral angle $n_pO_{(1)}-O_{(1)}-N-O_{(2)}$ in I ≈14° (the analogous angle in 1,3-dioxanes ≈26°), which is evidently sufficient for an $n-\sigma^*$ interaction. According to Fig. 4a, an increase in θ (CONO) is accompanied by an increase in the dihedral angle between $n_p(O)$ and n(N), which leads to the weakening of the repulsion of the UEP of the O and N atoms and thus stabilizes the molecule. In 1,3-dioxanes and acetals the $n-\sigma^*$ interaction leads to shortening

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[†] Here and subsequently, the numbering of the atoms corresponds to the numbering adopted in the x-ray diffraction study (Fig. 2).

[‡] In the ROX system the UEP of the O atom are nonequivalent, and the $n_p(O)$ highest occupied molecular orbital (HOMO) is perpendicular to the plane of the σ bonds of ROX [20].

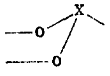
TABLE 2. Parameters of the ^{13}C NMR Spectra of Perhydro-1,3,2-dioxazines III and IV (90.81 MHz)

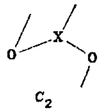
Compound	δ, ppm ($^nJ_{CH}$, Hz)					
	Me_2	C—N	MeO	$C_{(4)}$	$C_{(5)}$	C=O
III[a]	20,1 (^1J=129,4)	69,9 (^2J=3,7)	51,7 (^1J=146,1)	70,1 (^1J=144,3; ^2J=5,8)	32,2 (^1J=126,9; ^2J=3,7)	172,6 (^3J=3,7—3,8[b])
IV[c]	19,4; 19,9 (^1J=129,5)	69,6 (^2J=3,7)	52,6 (^1J=146,7)	75,9 (^1J=148,1; ^2J=5,7)	31,9 (^1J=127,6; ^2J=3,8)	173,2 (^3J=3,7—3,8[b])

[a] In C_6H_6, $\delta C_{(4)} = \delta C_{(6)}$. [b] The difference in $^3J_{CCCH}$ and $^3J_{COCH} \approx$ 0.1 Hz. [c] In $CDCl_3$. For 4-Me, δ 20.1 ppm, ^1J = 127.6 Hz, ^2J = 3.7 Hz; for $C_{(6)}$, δ 69.4 ppm, ^1J = 145.2 Hz, ^2J = 5.6 Hz.

of the C—O bonds by 0.02-0.05 Å as compared with ethers [16, 17] and to an anomalous increase in angle OCO [it is 114.3° in $(MeO)_2CH_2$ [21]]. The former is explained [16] by overlapping in the $n_pO_{(1)}—\sigma^*[C—O_{(2)}]$ phase (Fig. 4b), and the latter is explained by repulsion of the populated σ*(C—O) antibonding orbitals localized primarily on the C atom [4].

It is interesting to compare the average values of the N—O bond lengths in I (1.437 Å) and in N-alkoxy-1,2-oxazolidines [1.420 Å (endo) and 1.440 Å (exo) [4]].† A similar pattern is observed when one compares the average lengths of the C—O bonds in 1,3-dioxanes (1.416 Å [17]) and dimethoxymethane [1.382(4) Å [21]]. Thus shortening of the O—X bond in the (X = RN, R_2C) system is observed on passing from C_s symmetry (perhydro-1,3,2-dioxazines, 1,3-dioxanes) to C_2 symmetry (N-alkoxy-1,2-oxazolidines, acetals), i.e., the n—σ* interaction becomes more intense.


C_s


C_2

Consequently, it may be assumed that, in the absence of serious steric hindrance, dialkoxy amines and acetals have C_2 symmetry in solution and in the crystalline state.

The lengths of the C—O bonds in I [1.437(2) Å] are approximately the same as in N-alkoxy-1,2-oxazolidines [4] and perhydro-1,2-oxazine (1.446 Å [22]) and somewhat greater than in MeOEt (1.410 Å [25]). This lengthening is due to the inductive effect [26] — the increase in the p character of the orbitals of the C atom in the C—O bond under the influence of the electronegative N atom. The inductive effect of the O atoms also leads to the lengthening of the $N_{(1)}—C_{(4)}$ bond as compared with the average value of 1.47 A for the $N—Csp^3$ bond and to shortening of the $C—C_{(3)}$ bonds as compared with the C—C bonds in cyclohexane [1.536(1) Å [19]]. The strong thermal vibrations of the peripheral C atoms (Fig. 2) provide another possible reason for shortening of the C—C bonds. The character of the distortion of the bond angles at the $C_{(4)}$ atom [$N_{(1)}C_{(4)}C_{(5)}$ 113.7(2)°, $N_{(1)}C_{(4)}C_{(6)}$ 106.5(2)°, and $N_{(1)}C_{(4)}C_{(7)}$ 105.81(1)°] is explained, in analogy with [24], by stronger repulsion of the methyl group from the O atoms [Fig. 3, $N_{(1)} \rightarrow C_{(4)}$ projection] than from the UEP of the nitrogen atom. In the crystalline structure the $N_{(2)}—H_{(15)}\cdots O_{(3)}$ hydrogen bonds unite the molecules into chains directed along the z axis of the crystal. The structural parameters of the hydrogen bonds are as follows: $N_{(2)}—H_{(15)}$ 0.92 Å, $H_{(15)}\ldots O_{(3')}$ 2.03 Å,‡ angle $N_{(2)}H_{(15)}O_{(3)}$ 167(1)°, and angle $H_{(15)}C_{(3')}$-$C_{(8')}$ 164(1)°. The intermolecular contacts between the chains are greater than the sums of the van der Waals radii of the atoms [27].

EXPERIMENTAL

The NMR spectra were measured with Nicolet NT-360-WB (^1H 360 MHz, ^{13}C 90.81 MHz, tetramethylsilane as the internal standard) and Tesla BS-487-C (^1H 80 MHz) spectrometers. The

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† The N—O bond in I is stronger than in hydroxylamine (1.453 Å [2]), N-methylhydroxylamine hydrochloride (1.45 Å [23]), perhydro-1,2-oxazine (1.456 Å [24]), and N-methyl-1,2-oxazolidine [1.466(3) Å [5]].

‡ (x, 1/2 — y, z — 1.2).

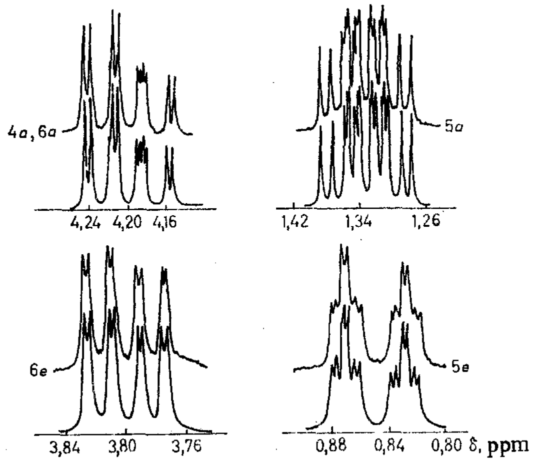

Fig. 1. Signals of the ring protons of perhydrodioxazine IV [360 MHz C_6D_6 {MeC(4)}]. The upper spectrum is the experimental spectrum, and the lower spectrum is the calculated spectrum.

TABLE 3. Coordinates of the Atoms (•10^4) in the I Molecule

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	3257 (1)	0934 (2)	1862 (1)	$H_{(1)}$	3209 (12)	2878 (26)	2352 (27)
$O_{(2)}$	2973 (1)	−0243 (2)	3375 (2)	$H_{(2)}$	3148 (10)	2206 (24)	0629 (25)
$O_{(3)}$	4509 (1)	2085 (2)	5376 (1)	$H_{(3)}$	2454 (10)	0646 (22)	1141 (24)
$N_{(1)}$	3470 (1)	0608 (2)	3279 (1)	$H_{(4)}$	2227 (11)	2186 (26)	1813 (27)
$N_{(2)}$	4383 (1)	3099 (2)	3339 (1)	$H_{(5)}$	2557 (9)	1479 (20)	3962 (21)
$C_{(1)}$	3121 (1)	2010 (3)	1605 (2)	$H_{(6)}$	2177 (10)	0132 (25)	3316 (25)
$C_{(2)}$	2542 (1)	1420 (3)	1842 (3)	$H_{(7)}$	4376 (11)	−2080 (27)	2881 (27)
$C_{(3)}$	2518 (1)	0739 (3)	3224 (3)	$H_{(8)}$	3716 (11)	−2224 (26)	2795 (28)
$C_{(4)}$	3956 (1)	−0316 (2)	3603 (2)	$H_{(9)}$	4014 (13)	−1274 (31)	1695 (31)
$C_{(5)}$	4005 (1)	−1589 (2)	2670 (3)	$H_{(10)}$	3563 (9)	−1401 (22)	5153 (22)
$C_{(6)}$	3885 (1)	−0763 (3)	5077 (2)	$H_{(11)}$	4230 (9)	−1211 (21)	5376 (21)
$C_{(7)}$	4482 (1)	0596 (2)	3409 (2)	$H_{(12)}$	3823 (9)	0089 (23)	5727 (26)
$C_{(8)}$	4458 (1)	1993 (2)	4138 (2)	$H_{(13)}$	4794 (8)	0066 (19)	3765 (19)
$C_{(9)}$	4303 (1)	4506 (2)	3888 (2)	$H_{(14)}$	4538 (7)	0777 (17)	2405 (18)
				$H_{(15)}$	4372 (8)	2967 (20)	2414 (21)
				$H_{(16)}$	4029 (12)	4514 (26)	4628 (28)
				$H_{(17)}$	4189 (12)	5128 (30)	3160 (3)

TABLE 4. Bond Lengths *l* (Å) in the I Molecule

Bond	l	Bond	l	Bond	l
$O_{(1)}-N_{(1)}$	1,435 (1)	$C_{(1)}-H_{(2)}$	0,98 (2)	$C_{(5)}-H_{(9)}$	1,01 (3)
$O_{(1)}-C_{(1)}$	1,434 (2)	$C_{(2)}-C_{(3)}$	1,509 (3)	$C_{(6)}-H_{(10)}$	0,98 (2)
$O_{(2)}-N_{(1)}$	1,440 (1)	$C_{(2)}-H_{(5)}$	1,02 (2)	$C_{(6)}-H_{(11)}$	0,97 (2)
$O_{(2)}-C_{(2)}$	1,443 (2)	$C_{(2)}-H_{(6)}$	1,00 (2)	$C_{(6)}-H_{(12)}$	1,05 (2)
$O_{(3)}-C_{(8)}$	1,228 (2)	$C_{(3)}-H_{(3)}$	1,03 (2)	$C_{(7)}-H_{(13)}$	0,97 (2)
$N_{(1)}-C_{(4)}$	1,491 (2)	$C_{(3)}-H_{(4)}$	1,05 (3)	$C_{(7)}-H_{(14)}$	1,01 (2)
$N_{(2)}-C_{(8)}$	1,330 (2)	$C_{(4)}-C_{(5)}$	1,529 (2)	$C_{(7)}-C_{(8)}$	1,517 (2)
$N_{(2)}-C_{(9)}$	1,461 (2)	$C_{(4)}-C_{(6)}$	1,522 (3)	$C_{(9)}-H_{(16)}$	0,98 (3)
$N_{(2)}-H_{(15)}$	0,92 (2)	$C_{(4)}-C_{(7)}$	1,540 (2)	$C_{(9)}-H_{(17)}$	0,97 (3)
$C_{(1)}-C_{(3)}$	1,510 (3)	$C_{(5)}-H_{(7)}$	1,02 (3)	$C_{(9)}-H_{(18)}$	0,99 (3)
$C_{(1)}-H_{(1)}$	1,13 (3)	$C_{(5)}-H_{(8)}$	0,93 (2)		

theoretical spectra of the ring protons of I-IV were calculated by means of the ITRCAL program with an NIC 1180-E minicomputer fitted with an NT-360-WB spectrometer.

The synthesis of II-IV was described in [3].

β-[2-(Perhydro-1,3,2-dioxazinyl)]isovaleric Acid Methylamide (I). A solution of 0.31 g (1.52 mmole) of methyl ester II in 3 ml of methylamine was maintained at 4°C in a sealed ampul for 12 days, after which the excess methylamine was removed, and the residue was recrystallized from CCl_4–hexane (1:3) to give 0.24 g (78%) of I with mp 97-98°C. Found: C 53.52; H 9.13; N 14.04%. $C_9H_{18}N_2O_3$. Calculated: C 53.48; H 8.97; N 13.95%.

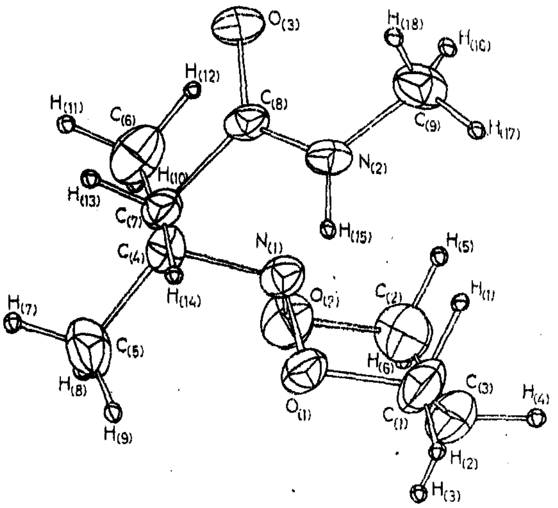

Fig. 2. The I molecule with 30% probability ellipsoids of the thermal vibrations of the nonhydrogen atoms.

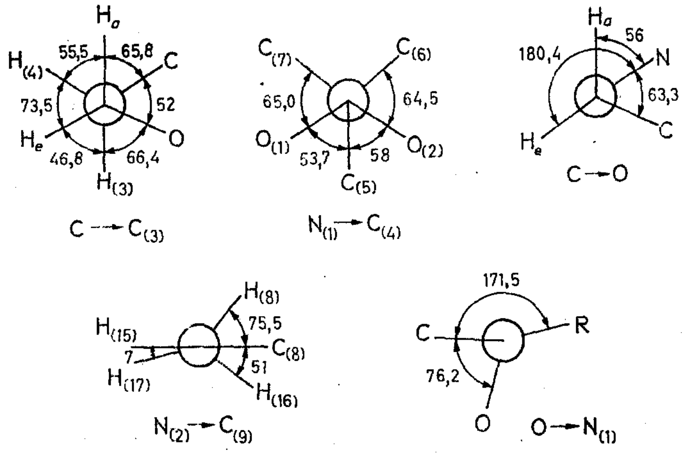

Fig. 3. Some dihedral angles in I from the results of x-ray diffraction analysis. The geometry was averaged with allowance for the plane of the symmetry passing through the $N_{(1)}$, $C_{(3)}$, $H_{(3)}$, and $H_{(4)}$ atoms.

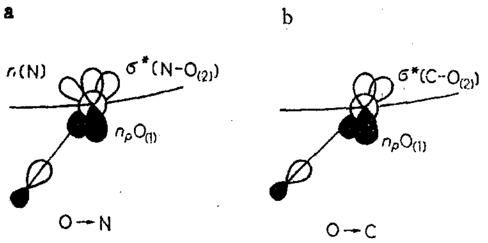

Fig. 4. Orientation of n(N), $n_p(O)$, and $\sigma^*(N-O)$ in the Newman projection in the O → N direction in perhydro-1,3,2-dioxane (a) and of (O) and $\sigma^*(C-O)$ in the O → C direction in 1,3-dioxane (b).

The white transparent crystals of I had the form of rectangular parallelepipeds stretched out along the c axis with rhombic syngony. The principal crystallographic data are as follows: $C_9H_{18}N_2O_3$, M = 190.180, a = 23.829(6), b = 9.555(2), c = 9.834(2) Å, V = 2238.6 Å^3, z = 8, d_{calc} = 1.132 g/cm^3, space group Pbca. The intensities of 1388 reflections with $I > 2\sigma$ were measured with a DAR-UM diffractometer.

Absorption was disregarded [$\mu(Cu\ K_\alpha) = 6.5\ cm^{-1}$]. The structure was decoded by the direct method [28]. The H atoms were localized from R syntheses. The structure was refined by the

TABLE 5. Bond Angles ω (deg) in the I Molecule

Angle	ω	Angle	ω	Angle	ω
$N_{(1)}O_{(1)}C_{(1)}$	105,3 (1)	$N_{(1)}C_{(4)}C_{(7)}$	105,8 (1)	$C_{(1)}C_{(3)}H_{(3)}$	110 (1)
$N_{(1)}O_{(2)}C_{(2)}$	104,1 (1)	$C_{(5)}C_{(4)}C_{(6)}$	110,9 (2)	$C_{(1)}C_{(3)}H_{(4)}$	113 (1)
$O_{(1)}N_{(1)}O_{(2)}$	105,3 (1)	$C_{(5)}C_{(4)}C_{(7)}$	108,3 (2)	$C_{(2)}C_{(3)}H_{(3)}$	107 (1)
$O_{(1)}N_{(1)}C_{(4)}$	105,3 (1)	$C_{(6)}C_{(4)}C_{(7)}$	111,6 (2)	$C_{(2)}C_{(3)}H_{(4)}$	107 (1)
$O_{(2)}N_{(1)}C_{(4)}$	106,9 (1)	$C_{(4)}C_{(5)}H_{(7)}$	108 (1)	$H_{(3)}C_{(3)}C_{(4)}$	110 (2)
$C_{(8)}N_{(2)}C_{(9)}$	122,1 (1)	$C_{(4)}C_{(5)}H_{(8)}$	113 (2)	$N_{(1)}C_{(4)}C_{(5)}$	113,7 (2)
$C_{(8)}N_{(2)}H_{(15)}$	119 (1)	$C_{(4)}C_{(5)}H_{(9)}$	110 (2)	$N_{(1)}C_{(4)}C_{(6)}$	106,5 (2)
$C_{(9)}N_{(2)}H_{(15)}$	119 (1)	$O_{(2)}C_{(2)}C_{(3)}$	110,2 (2)	$C_{(4)}C_{(7)}C_{(8)}$	114,1 (1)
$O_{(1)}C_{(1)}C_{(3)}$	108,9 (2)	$O_{(2)}C_{(2)}H_{(5)}$	108 (1)	$C_{(4)}C_{(7)}H_{(13)}$	107 (1)
$O_{(1)}C_{(1)}H_{(1)}$	107 (1)	$O_{(2)}C_{(2)}H_{(6)}$	103 (1)	$C_{(4)}C_{(7)}H_{(14)}$	109 (1)
$O_{(1)}C_{(1)}H_{(2)}$	105 (1)	$C_{(3)}C_{(2)}H_{(5)}$	110 (1)	$C_{(8)}C_{(7)}H_{(13)}$	109 (1)
$C_{(3)}C_{(1)}H_{(1)}$	110 (1)	$C_{(3)}C_{(2)}H_{(6)}$	111 (1)	$C_{(8)}C_{(7)}H_{(14)}$	108 (1)
$C_{(3)}C_{(1)}H_{(2)}$	106 (1)	$H_{(5)}C_{(2)}H_{(6)}$	114 (2)	$H_{(13)}C_{(7)}H_{(14)}$	110 (2)
$H_{(1)}C_{(1)}H_{(2)}$	119 (2)	$C_{(1)}C_{(3)}C_{(2)}$	109,5 (2)	$C_{(7)}C_{(8)}O_{(3)}$	121,9 (2)

method of least squares within the total-matrix approximation with allowance for the anisotropy for the C, N, and O atoms and for the isotropy for the H atoms up to R = 0.046. The coordinates of the atoms are presented in Table 3, the bond lengths are given in Table 4, and the bond angles are presented in Table 5. Figure 2 was obtained by means of the ELLIDS program [29].

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STEREOSPECIFICITY OF THE $^3J_{CH}$ SPIN–SPIN COUPLING CONSTANTS IN BICYCLIC cis-DIAZIRIDINES. STEREOCHEMISTRY OF 2,4,6-TRIALKYL-1,3,5-TRIAZABICYCLO[3.1.0]HEXANES*

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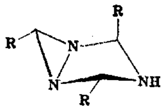
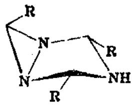
Stereospecificity of the $^3J_{C,N,C,H}$ spin–spin coupling constants ($^3J^{trans} > J^{gauche}$) in the ^{13}C NMR spectra of 1,5-diaza- and 1,3,5-triazabicyclo[3.1.0]hexanes was observed. Proceeding from this, the preferred conformations of the d,*l* and meso isomers of 2,4,6-trialkyl-1,3,5-triazabicyclo[3.1.0]hexanes were established, and a mechanism for the interconversion of these isomers via openings of the five-membered ring and an imino-enamine equilibrium was proposed. It is also shown that the stereochemical result of the Schmitz reaction is determined in the step involving cyclization of the iminium intermediate.

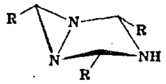
2,4,6-Trialkyl-substituted 1,3,5-triazabicycle[3.1.0]hexanes (TABH), which are formed by the action of NH_3 and chloramine on aldehydes (the Schmitz reaction [2, 3]) or in the chlorination of 2,4,6-trialkyl-1,3,5-triazans [3], exist in the form of one d,*l* isomer (a) and two meso isomers (b, c). The preferred "chair" conformation and an endo orientation of the methyl group in the 6 position in the least populated isomer (b) are proposed for all three isomers [3]. We have previously proposed an alternative boatlike conformation for the d,*l* and two meso isomers (Ia-c) of 2,4,6-trimethyl-1,3,5-triazabicyclo[3.1.0]hexane proceeding from the assumption of the common character of the mechanism of the formation of 1,5-diazabicyclo-[3.1.0]hexanes (DABH) and TABH and the common character of the factors that stabilize the boat form and on the basis of the results of the x-ray diffraction analysis of Ia [4].



a



b



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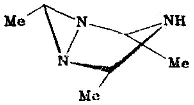

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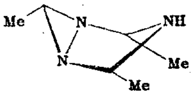

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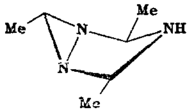

Ic

R=CH_3; C_2H_5; C_3H_7; $(CH_3)_2CH$; C_4H_9; $C_2H_5(CH_3)CH$; C_5H_{11}; C_6H_{13}

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*Communication 42 from the series "Asymmetric unbridged nitrogen." See [1] for communication 41.

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