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Cyclopolymerization. V. The ^{13}C Spectrum and Structure of the Low Molecular Weight Product from the Reaction of N-Methyl-N,N-diallylamine with Azobisisobutyronitrile

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ABSTRACT

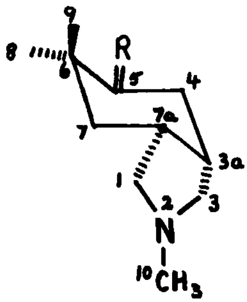
A study of the ^{13}C chemical shift data and of the shifts induced by Eu(dpm)$_3$ has shown that the aminoketone formed in the reaction of N-methyl-N,N-diallylamine with cyanoisopropyl radicals is 2,6,6-trimethyl-cis-perhydroisoindolid-5-one (1a, R = O). The ^{13}C NMR spectrum in the presence of acid reveals the existence of two protonated forms of this compound.

INTRODUCTION

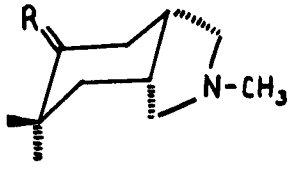
^{13}C Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for the determination of structure and conformation of organic compounds. Chemical shift data and lanthanide-induced shifts have been used to assign both the structure and conformation of the aminoketone formed in the reaction of N-methyl-N,N-diallylamine with cyanoisopropyl radicals [1]. The amine, formed from the aminoketone by Wolff-Kishner reduction [1], has been used for these NMR studies.

RESULTS AND DISCUSSION

The reaction of N-methyl-N,N-diallylamine with cyanoisopropyl radicals, generated by the thermolysis of azobisisobutyronitrile, gives an aminoketone, $C_{11}H_{19}NO$ [1], which, depending upon whether the initial reaction with the cyanoisopropyl radical and subsequent cyclization involves attack at the β-carbons and/or the γ-carbons, can have one of the five structures (1-5, R = O). The cis-perhydroisoindolidone structure (1, R = O) can exist in one of the two possible conformations (1a or 1b, R = O) or as an equilibrium mixture of both. Wolff-Kishner reduction of the aminoketone affords an amine [1], with the corresponding possible structures (1-5, R = H_2). The ^{13}C NMR spectrum of the amine measured in $CDCl_3$ solution, with proton-noise decoupling (Fig. 1a) consists of eleven individual signals corresponding to the eleven different carbon atoms. The nonequivalence of all the carbons indicates a lack of symmetry in the molecule and excludes the structure (3, R = H_2) since this structure has a plane of symmetry such that the carbons 1 and 3, 3a and 4a, and 5 and 7 are equivalent. Single-frequency off-resonance proton decoupling can be used to determine the substitution at a particular carbon as the residual couplings correspond to proton-carbon couplings from directly bound nuclei [2]. Under these decoupling conditions, methyl carbons resonate as quartets, methylene carbons as triplets, methine carbons as doublets, and fully substituted carbons as singlets. The off-resonance decoupled spectrum of the amine (Fig. 1b) has methyl signals at 25.9, 32.5, and 43.2 ppm; methylene signals at 22.7, 35.0, 41.3, 59.3, and 63.3 ppm; methine signals at 35.0 and 36.9 ppm; and a fully substituted carbon signal at 29.8 ppm. The 43.2 ppm methyl signal can be assigned to the N-methyl group and the chemical shift is consistent with a pyrrolidine N-methyl (42.9 ppm) rather than a piperidine (47.9 ppm) or a seven-membered nitrogen ring (48.2 ppm) [3]. The other two methyl signals are assigned to the geminal dimethyl group, the lower field signals at 32.5 ppm to the equatorial methyl, and the higher field at 25.9 ppm to the axial methyl [4]. These chemical shifts are in excellent agreement with the reported shifts for the geminal dimethyl group in 1,1,3-trimethylcyclohexane (34.3 and 25.5 ppm) in contrast to the shifts reported for 1,1,2-trimethylcyclohexane (31.1 and 19.7 ppm) [4]. The chemical shift of the fully substituted carbon (29.8 ppm) assigned to the carbon bearing the geminal dimethyl group is also in agreement with the shift of the respective carbon in 1,1,3-trimethylcyclohexane



(1a)



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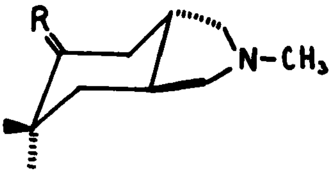

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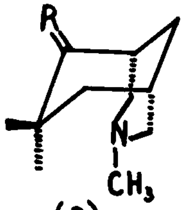

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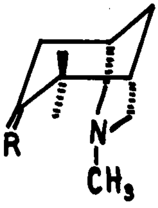

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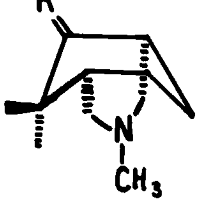


(5)

(31.4 ppm) rather than the 1,1,2-derivative (33.5 ppm) [4]. These data would suggest structures (1 or 2, R = H_2) rather than structures (4 or 5, R = H_2) for the amine as the former incorporate an N-methyl pyrrolidine moiety and a geminal dimethyl group having a β-alkyl substituent and no α-alkyl substituent. Dalling and Grant [4] have investigated an extensive series of methyl-substituted cyclohexane derivatives and have derived a set of methyl substituent parameters from which the ^{13}C shifts of the ring carbons can be calculated. The theoretical shifts for 1,1,3eq,4ax-;

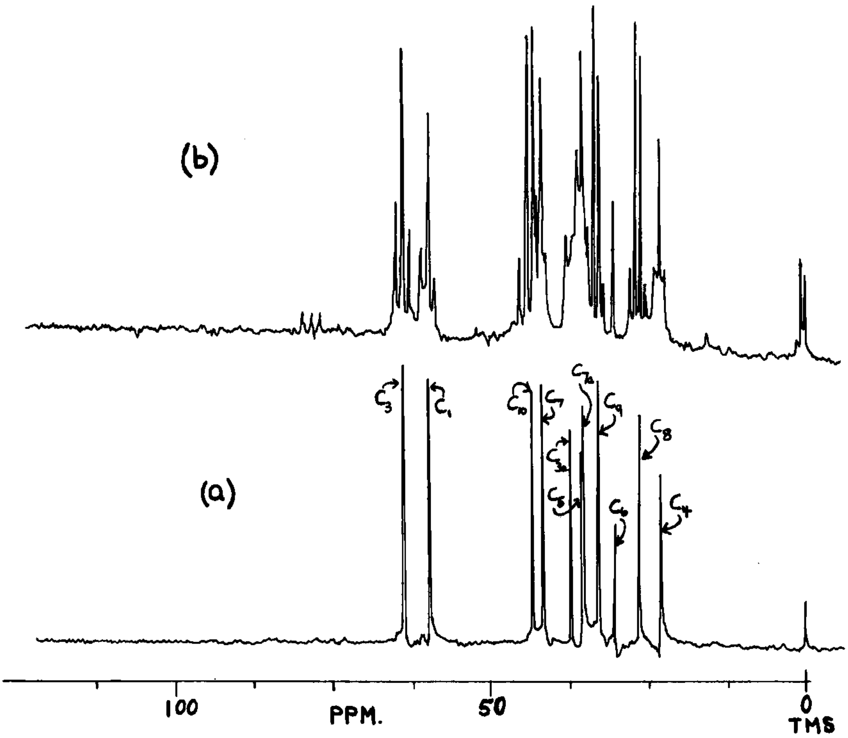


FIG. 1. (a) ^{13}C Proton noise decoupled spectrum of 2,6,6-trimethyl-cis-perhydroisoindole (1a, R = H_2) in $CDCl_3$. (b) ^{13}C Single frequency off-resonance proton decoupled spectrum of 2,6,6-trimethyl-cis-perhydroisoindole (1a, R = H_2) in $CDCl_3$.

1,1,3ax,4eq-; 1,1,3eq,4eq-; 1,1,3ax,5ax-; 1,1,2ax,4ax-; and 1,1,2ax,5ax-tetramethylcyclohexane have been calculated from these empirical parameters and shifts are recorded in Table 1. Comparison of these shifts with the experimental values for the amine rules out all structures except (1) and (2) which further supports a perhydroisoindole structure for the amine. When consideration is given to the shielding effect of the nitrogen, a correction to the γ-carbons, viz., carbons 4 and 7, of -4.6 ppm [5] should be applied. The resulting calculated values for the shifts of the structure (1a) are in good agreement with the experimental figures (Table 1). If structure (1a) is the conformation of the amine, the equilibrium between the cis-conformations (1a) and (1b) must lie predominantly toward (1a).

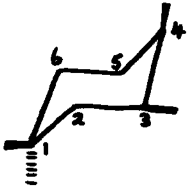
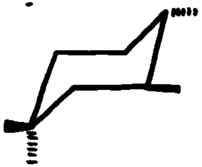
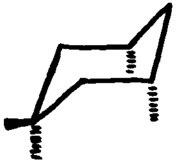
Inspection of Drieding molecular models supports this proposal as severe 1,3-diaxial steric interactions between the C6 axial methyl and the C7 axial substituent are evident in the conformation (1b). The chemical shifts of the signals assigned to the methylene carbons α to the nitrogen atom at 59.3 and 63.3 ppm indicate a cis rather than trans ring junction. Both shifts are to lower field than that reported for the α-methylene carbon signal of N-methyl pyrrolidine (56.9 ppm) [3], but this would be expected from the substitution at the β-carbon atoms. That the shifts are different reflects the cis-ring junction, whereby one β-substituent has an equatorial configuration and hence a larger shift than the other with an axial configuration [4]. With the predicted structure (1a) the lower field signal at 63.3 ppm can be assigned to the C3-methylene carbon and the higher field signal at 59.3 ppm to the C1-methylene. This chemical shift difference is in excellent agreement with the 3.8 ppm difference reported for axial and equatorial methyl substituents [4] in substituted cyclohexanes.

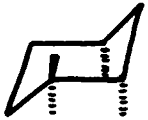
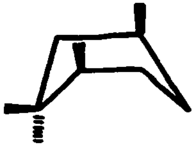
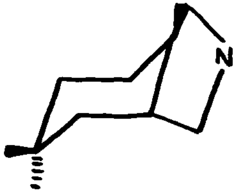
Lanthanide-induced shifts have a dipolar mechanism which has both a distance and angular dependence. Extensive use has been made of such reagents, both qualitatively and quantitatively, in structural and stereochemical studies [6], but most applications have been in proton NMR spectroscopy. Because of the overlapping of signals in the proton NMR of complex organic molecules, it is not always possible to analyze these spectra. By contrast, the chemical shifts of carbon NMR spectra, under noise-decoupling conditions, can be readily determined as all the signals resonate as singlets. Recent reports have shown that contact terms also contribute to the induced shifts in the carbon spectra, particularly at the carbon atoms α and β to the coordinated heteroatom [7]. Being aware of this complication an attempt has been made to distinguish between the cis-(1a) and trans-(2) structures of the amine by a quantitative study using tris(dipivoylmethanato)europium [$Eu(dpm)_3$] as the reagent. Induced shifts of the individual carbon signals were measured at a number of $Eu(dpm)_3$ concentrations and the experimental shifts at an equimolar ratio (Table 2) calculated by extrapolation using a least-squares program.

The coordinates of the individual carbon atoms were measured from Drieding models and the molecule translated and rotated such that the nitrogen was located at the origin of a Cartesian coordinate system, carbon 1 on the z-axis and carbon 7a in the xz plane. The metal was defined by the polar coordinates (r, θ, ϕ) which were incremented to optimize for minimum total error between the observed and calculated shifts using the axially symmetric dipolar expression $(3\cos^2\chi - 1)/r^3$ [8] where χ is the angle between the principal magnetic axis of the complex and the distance vector, r, joining the metal and the carbon under consideration. The principal magnetic axis has been assumed to be collinear with the nitrogen to metal bond as the results of Roberts and his co-workers [9] have shown insignificant deviations

TABLE 1. ^{13}C Chemical Shifts of Substituted Cyclohexanes

Calculated Shifts[a]

	C_1	C_2	C_3	C_4	C_5	C_6
	30.9	44.1	33.1	37.3	27.5	34.9
	25.3	45.8	32.3	38.1	23.5	40.5
	30.7	49.5	34.5	39.5	31.2	40.3
	20.2	45.7	18.0	37.7	18.0	45.7

	29.8	36.1	36.3	32.7	23.0	27.4
	30.8	41.6	22.1	27.1	23.3	40.4
	30.9	39.7	33.1	37.3	21.9	34.9
	Experimental Shifts[b]					
	29.8	41.3	35.0	36.9	22.7	35.0

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[a] Using the methyl parameters of Dalling and Grant [4] and a γ-shielding of -4.6 ppm from nitrogen [5].

[b] Numbered to correspond with the cyclohexane numbering.

TABLE 2. Experimental and Calculated Lanthanide Induced Shifts of Perhydroisoindoles (1a and 2, R = H_2)

Carbon	Experimental[a] (ppm)	Calculated for 1a[b] (ppm)	Calculated for 2[c] (ppm)
3a	18.8	17.3	17.8
4	5.4	5.4	5.4
5	5.0	5.3	4.8
6	5.0	5.2	5.3
7	10.9	10.5	8.6
7a	15.6	17.2	17.5
8	3.7	3.0	3.7
9	2.2	2.7	3.8

[a] Obtained by extrapolation to 1:1 molar ratio $Eu(dpm)_3$:Amine.
[b] Using minimum error metal coordinates (2.5 Å, 122°, 235°).
[c] Using minimum error metal coordinates (2.5 Å, 155°, 275°).

from collinearity when the axis is allowed to vary. Because of the likely contact contributions at the carbons α to the nitrogen, the carbons 1, 3 and 11 were deleted from the calculations. As would be expected, similar errors (Table 2) have been obtained from both the cis-(1a) and trans-(2)-structure calculations as the eight carbons used make up the geminal dimethylcyclohexane moiety of each structure and as such have almost identical orientations with respect to each other. The calculated minimum error position of the metal atom is, however, significant as in the cis-structure (1a) the calculated metal coordinates (2.5 Å, 122°, 235°) is a chemically likely position with the large metal atom in the sterically least hindered region. By contrast the calculated position of the metal in the trans-structure (2) at (2.5 Å, 155°, 275°) is chemically unlikely with a large C1-N-metal bond angle of 155°, and is in a sterically hindered region. Although not conclusive, these results support the previous chemical shift data that the amine is 2,6,6-trimethyl-cis-perhydroisoindole (1a, R = H_2).

The ^{13}C NMR shift data for the aminoketone (Fig. 2) are in complete accord with the perhydroisoindolidone structure (1a, R = O). A carbonyl signal at 212.7 ppm is consistent with a geminal dimethyl group substituent on the β-carbon as this would produce a downfield shift of 4 ppm from the carbonyl signal of cyclohexanone at 208.8 ppm [10]. Although no precise carbonyl shielding parameters are available for the

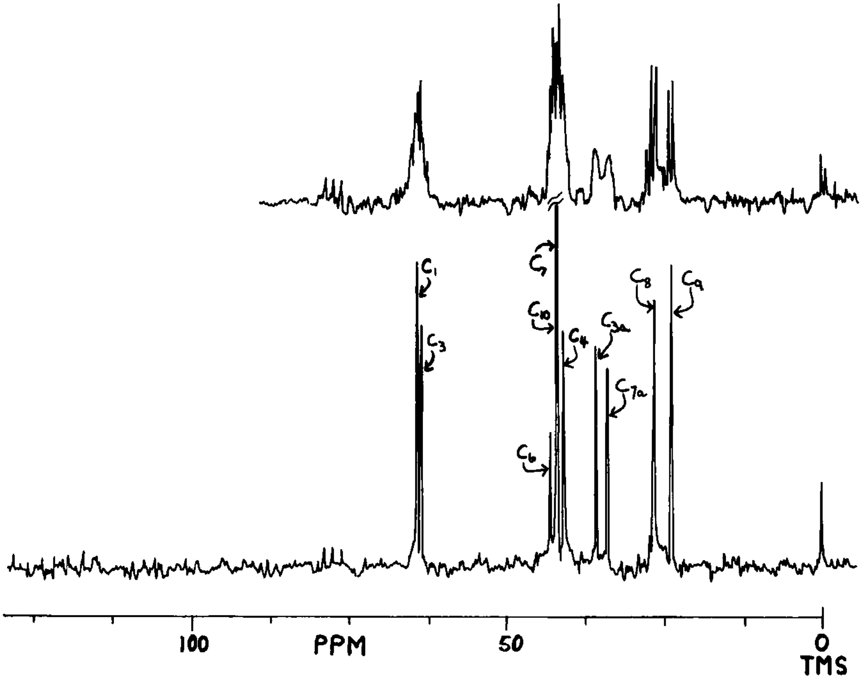


FIG. 2. ^{13}C NMR spectrum of 2,6,6-trimethyl-cis-perhydroiso-indolid-5-one (1a, R = O) in $CDCl_3$.

system under study, a large downfield shift for the α-carbons and smaller upfield shifts for the β- and γ-carbons could be expected [11]. The experimental shifts of the geminal dimethylcyclohexanone moiety are in qualitative agreement with these predictions. The α-carbons C4 and C6 undergo downfield shifts of 18.3 and 12.9 ppm, respectively, to 40.8 and 42.8 ppm while the β-carbons C3a, C8, and C9 undergo smaller upfield shifts of 1.4, 6.1, and 2.2 ppm, respectively, to 35.6, 26.4, and 23.7 ppm. Although the other β-carbon, C7, undergoes a small downfield shift of 0.6 to 41.9 ppm, the only γ-carbon, C7a, has the expected upfield shift of 1.3 to 33.7 ppm. The methylene carbons C1 and C3, at 63.2 and 63.9 ppm, respectively, are more equivalent in the aminoketone than in the amine, and this reflects the conformational change in the six-membered ring due to the carbonyl group. The conformational change is such that the β-substituents, equatorial and axial in the amine, are now more nearly equivalent even with the cis-ring junction.

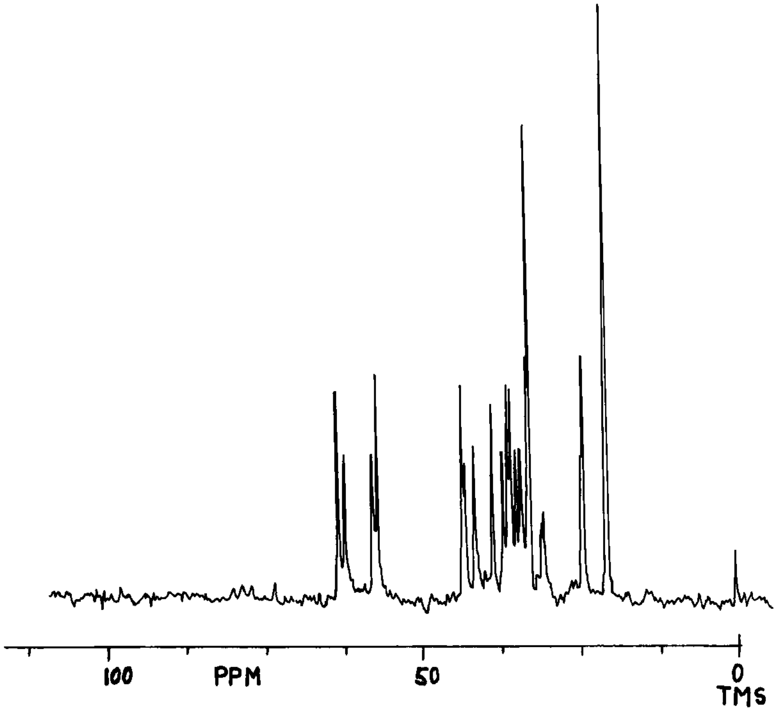
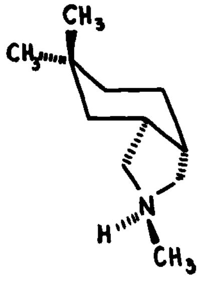


FIG. 3. ^{13}C Proton noise decoupled spectrum of 2,6,6-trimethyl-cis-perhydroisoindole in $CDCl_3$ containing trifluoroacetic acid.

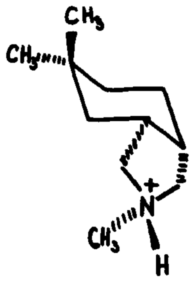
The N-methyl signal at 41.9 ppm is in agreement with the proposed N-methyl pyrrolidine structure.

In both the amine (1a, R = H_2) and the aminoketone (1a, R = O) there is no conformational preference of the N-methyl group and the nitrogen undergoes rapid inversion. This is clearly demonstrated by the existence of two protonated forms of both compounds in the ^{13}C spectra when measured in $CDCl_3$ in the presence of trifluoroacetic acid. The noise-decoupled spectrum of the amine (Fig. 3) is comprised of 22 distinct signals corresponding to the 11 carbons of each protonated form (6a) and (6b).

The proportion of each compound is not the same but rather a ratio of approximately 7:5 is observed. As would be expected, the largest shift difference occur at those carbons α and β to the nitrogen atom, the same carbons that undergo the largest upfield shifts on protonation.



(6a)



(6b)

Although this same effect is observed in the N-methyl signals of the proton NMR spectrum (the N-methyl protons resonate as an overlapping pair of doublets), the effect is not obvious in the other proton signals. These results clearly show the power of the ^{13}C NMR technique in determining minor changes in structure of organic molecules.

EXPERIMENTAL

^{13}C NMR spectra were measured on approximately 20% solution in $CDCl_3$ on an HX90 Bruker spectrometer operating at 22.6 MHz in the pulsed mode. Chemical shifts are reported in ppm downfield from tetramethylsilane (0.0 ppm). Lanthanide-induced shifts were obtained by the addition of weighed amounts of $Eu(dpm)_3$ to a weighed sample of amine in $CDCl_3$. Shifts at a 1:1 ratio $Eu(dpm)_3$:amine were obtained by extrapolation using a linear least-squares program to give the values shown in Table 3.

The coordinates of the individual carbon atoms of structures (1a) and (2) were measured from Drieding models, and the molecule translated and rotated such that the nitrogen was located at the origin, C1 on the z axis and C7a in the xz plane of a Cartesian coordinate system. The coordinates shown in Table 4 were obtained.

Using the axially symmetric dipolar relationship $(3 \cos^2 \chi - 1)/r^3$ and the carbons C3a, C4, C5, C6, C7, C7a, C8, and C9, the polar coordinates of the lanthanide (r, θ, ϕ) were incremented to optimize for the minimum total error for each structure. The shifts for the best geometry are reported in Table 2.

TABLE 3. Lanthanide-Induced Shifts Obtained by Extrapolation to 1:1 Molar Ratio $Eu(dpm)_3$:Amine

Carbon	ppm (corr coeff)
1	69.5 (.997)
3	68.2 (.997)
3a	18.8 (.997)
4	5.4 (.995)
5	5.0 (.981)
6	5.0 (.997)
7	10.9 (.994)
7a	15.6 (.997)
8	3.7 (.994)
9	2.2 (.970)
10	85.3 (.998)

TABLE 4. Coordinates of Carbon Atoms

Carbon	Structure 1a coordinates	Structure 2 coordinates
1	0, 0, 1.54	0, 0, 1.48
3	1.42, 0.05, -0.5	1.26, 0.57, -0.51
3a	2.19, -0.63, 0.72	1.94, 1.06, 0.81
4	3.66, -0.23, 0.62	3.46, 1.14, 0.88
5	3.85, 1.3, 0.62	3.77, 1.66, 2.35
6	3.44, 1.74, 2.02	3.30, 0.66, 3.38
7	1.87, 1.55, 2.10	1.76, 0.55, 3.31
7a	1.48, 0, 1.93	1.47, 0, 1.90
8	3.76, 3.22, 2.21	3.78, 1.04, 4.77
9	4.11, 0.84, 3.09	3.92, -0.75, 3.0
N	0, 0, 0	0, 0, 0

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