Conformational Analysis by Nuclear Magnetic Resonance Spectroscopy. N′ Derivatives of *N*-Aminocamphorimides

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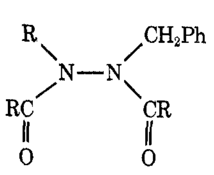
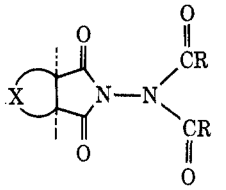
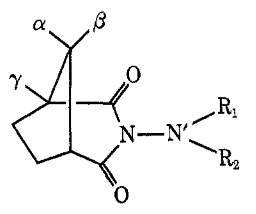
A series of N′ derivatives of *N*-aminocamphorimide has been prepared and characterized by ir and nmr spectroscopy. The nmr spectra studied at 44.5° provide evidence for the preferred conformations due to restricted rotation about the N–N′ or the N′–CO bond. The nonplanar "cage moiety," *i.e.*, the camphorimidyl system, has been used for the conformational study of the substituents at the exocyclic nitrogen atom. The spectra of *N*′-monoacyl derivatives which are characterized by the shielding constants of the β-methyl group of the "cage moiety" show restricted rotation about the N′–CO bond. N′-Disubstituted derivatives strongly prefer noneclipsed conformations due to restricted rotation about the N–N′ bond. Barriers to free energy of activation, $\Delta G^{\ddagger}$, have been determined by temperature-dependent spectral measurements.

It can be shown from the available experimental details that the conformations adopted by substituted hydrazines depend upon the nature of the substituents.[1–4] Preferred conformations of certain acyclic *N*,*N*′-diacylhydrazines (I)[3] and other related systems[1,2] have been reported to be due to restricted rotation about the N–N and N–CO bonds. Similar observations of restricted rotation about the N–N bond have been reported for tetraacylhydrazines (II).[4] The existence of nonplanar ground states has been proposed in all these systems. The present study reports evidence for the conformations adopted by N′ substituents in a series of *N*-aminocamphorimide derivatives (IIIa–IIIm). Nmr spectra of some of the representative derivatives recorded at 44.5° are discussed on the basis of slow rotation about the N′–CO and N–N′ bonds, the free energies of activation ($\Delta G^{\ddagger}$) being calculated from the variable-temperature spectra using Eyring's rate equation.[5]


I


X represents a chain of four carbon atoms

II



IIIa, $R_1 = R_2 = H$
b, $R_1 = COCH_3$; $R_2 = H$
c, $R_1 = COPh$; $R_2 = H$
d, $R_1 = m\text{-}COC_6H_4CH_3$; $R_2 = H$
e, $R_1 = CO_2C_2H_5$; $R_2 = H$
f, $R_1 = COC_2H_5$; $R_2 = H$
g, $R_1 = COCF_3$; $R_2 = H$
IIIh, $R_1 = Ph$; $R_2 = H$
i, $R_1 = 2,4\text{-}C_6H_3(NO_2)_2$; $R_2 = H$
j, $R_1 = R_2 = COCH_3$
k, $R_1 = Ph$; $R_2 = COCH_3$
l, $R_1 = R_2 = CH_2Ph$
m, *N*,*N*′-Biscamphorimidyl

Flautt and Erman,[6] in their studies on the stereochemistry of substituted bornanes with nmr spectroscopy, observed no clear pattern of the shielding constants of the three methyl groups with respect to the stereochemistry of the substituents. Nakagawa, *et al.*,[7] correlated the shielding constants of the three methyl groups of the pinane derivatives and the magnetic anisotropy of the cyclobutane system with the puckered structure. A similar approach in the present system has been made to correlate the shielding constants of the three methyl groups with the conformations of N′ substituents. The shielding constants of the β-methyl of the cage structure are affected by the N′ substituents, whereas those of α- and γ-methyls are not much affected. Chemical shifts of the three methyl groups (α, β, and γ) of the compounds IIIa–IIIm are recorded in Table I.

***N*′-Monoacyl-*N*-aminocamphorimides.**—The three methyl groups of camphorimide and *N*-anilinocamphorimides (IIIh and IIIi) appear as three signals, each of 3 H intensity, in the nmr spectrum (δ 1.00–1.25). On the other hand, monoacylsubstituted compounds (IIIb–IIIf) show a characteristic type of spectra: two sharp signals (each of 4.5 H intensity) around δ 1.00 and 1.25 in $CDCl_3$, accounting for nine protons of the three methyl groups of the camphorimidyl moiety (Figure 1, Table I). This behavior of monoacyl derivatives could not be explained on the basis of accidental overlap of the signals, as has been observed in some camphorimide derivatives. For example, the spectrum of the compound IIIa shows only two sharp signals for the three methyl groups with relative intensities of 3 H and 6 H (Table I). This type of accidental overlap could be removed by taking advantage of "solvent shifts" in aromatic solvents. Thus, in benzene the three methyl groups of IIIa resonate at δ 0.71 (3 H), 0.81 (3 H), and 1.10 (3 H), respectively.

The spectra of the compounds IIIb–IIIf indicate the possibility of two equally populated conformations, both being stable with respect to the nmr time scale. In the two conformations, the β-methyl (in III) point-

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[1] J. C. Breliere and J. M. Lehn, *Chem. Commun.*, No. 18, 426 (1965); J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, **89**, 81 (1967); *Tetrahedron*, No. 1, **24**, 123, 137 (1968).

[2] B. J. Price, R. V. Smallman, and I. O. Sutherland, *Chem. Commun.*, No. 11, 319 (1966); B. J. Price, I. O. Sutherland, and F. G. Williamson, *Tetrahedron*, No. 10, **22**, 3477 (1966); R. Daniels and K. A. Roseman, *Tetrahedron Lett.*, No. 13, 1335 (1966); M. J. S. Dewar and W. B. Jennings, *J. Amer. Chem. Soc.*, **91**, 3655 (1967).

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[4] B. H. Korsch and N. V. Riggs, *Tetrahedron Lett.*, **No. 47**, 5897 (1966).

[5] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); L. W. Reeves in "Advances in Physical Organic Chemistry," Vol. 3, V. Gold, Ed., Academic Press, New York, N. Y., 1965, Chapter 4.

[6] T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963).

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Table I

Chemical Shifts of the Three Methyl Groups of N′ Derivatives of *N*-Aminocamphorimide (with Proton Count in Parentheses) in $CDCl_3$ at 44.5°

Compd	δ, ppm from internal TMS reference			
Camphorimide	1.00 (3 H)	1.05 (3 H)	1.20 (3 H)	
IIIa	0.98 (6 H)	1.25 (3 H)		
IIIb	1.00 (4.5 H)	1.25 (4.5 H)		
IIIc	1.00 (4.5 H)	1.25 (4.5 H)		
IIId	1.00 (4.5 H)	1.23 (4.5 H)		
IIIe	1.02 (4.5 H)	1.25 (4.5 H)		
IIIf	1.00 (4.5 H)	1.20 (4.5 H)		
IIIg	0.97 (3 H)	1.03 (1.5 H)	1.16 (1.5 H)	1.25 (3 H)
IIIh	1.00 (3 H)	1.05 (3 H)	1.22 (3 H)	
IIIi	1.15 (3 H)	1.18 (3 H)	1.31 (3 H)	
IIIj	1.05 (3 H)	1.30 (6 H)		
IIIk	0.80 (1.5 H)	0.99 (3 H)	1.23 (3 H)	1.43 (1.5 H)
IIIl	0.70 (3 H)	0.78 (3 H)	1.06 (3 H)	
IIIm	1.01 (6 H)	1.23 (6 H)	1.31 (6 H)	

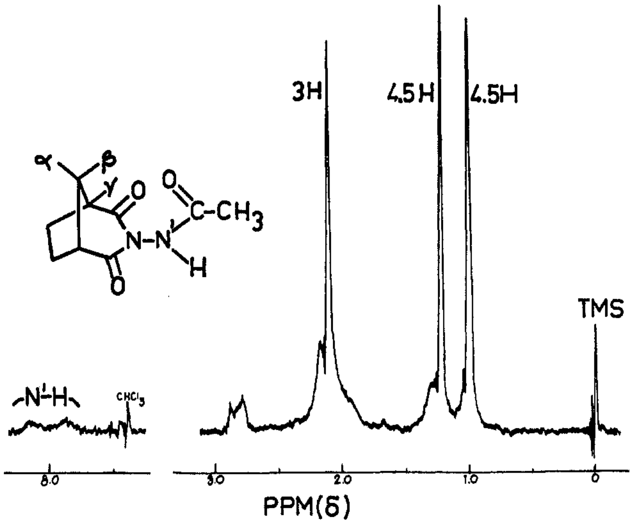

Figure 1.—60-MHz nmr spectrum of *N*′-acetyl-*N*-aminocamphorimide (IIIb) in $CDCl_3$ at 44.5°.

ing toward the N–N′ bond could acquire two different magnetic environments, more or less like those of α- and γ-methyls. In consequence, the β-methyl resonance distributes itself between those of α- and γ-methyls, giving rise to two singlets of equal intensity. The N′H resonance appearing as a broad doublet of equal intensity also supports the possibility of two conformations (Figure 1, Table II). This is further evidenced by the appearance of four signals of relative intensities 1.5:3:1.5:3 (Figure 2) for the three methyl groups when the spectra of these compounds are recorded in aromatic solvents. A more pronounced effect on the β-methyl is seen when the substituent is $COCF_3$ (compound IIIg) where it appears as two singlets, each of 1.5 H intensity even in $CDCl_3$.

The possibility of two conformations due to intramolecular hydrogen bonding[8] between N′–H and one of the imidyl carbonyls is excluded because such conformations would not allow the β-methyl to experience significantly different environments. Moreover, on this basis, other monosubstituted derivatives, *e.g.*, IIIh and IIIi, should also be expected to give similar observations but they show no multiplicity for any of the cage methyls (Table I).

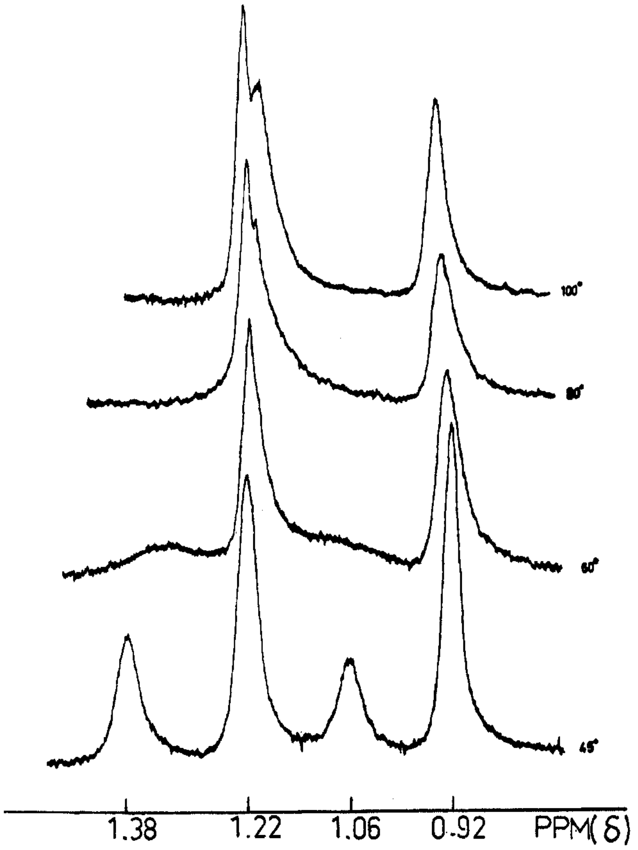

Figure 2.—Spectra of methyl signals of *N*′-acetyl-*N*-aminocamphorimide (IIIb) in nitrobenzene at different temperatures.

Molecular models show that the magnetic environment of the β-methyl (syn to the N–N′ bond) would be sensitive toward the rotational changes in the substituents at the exocyclic nitrogen atom. Different conformations could arise due to some hindered internal rotation in the molecule which may be either (i) about the N–N′ bond or (ii) about the N′–CO bond. Two conformations due to restricted rotation about the N–N′ bond would very likely show two signals for the acetyl methyl (in IIIb), because of the nonsymmetric cage structure, which provides different magnetic environment for the acetyl methyl in the different conformations. It is evident from the spectrum of *N*′,*N*′-diacetyl-*N*-aminocamphorimide (IIIj), where two

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[8] J. P. Chupp and A. J. Speziale, *J. Org. Chem.*, **28**, 2592 (1963).

TABLE II

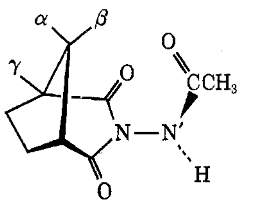
MELTING POINTS, CHARACTERISTIC INFRARED PEAKS, AND NMR OF IIIa–IIIm

			Ir data,[a] cm^{-1}		Nmr data,[b] δ			
							N′ substituents	
No.	Compd	Mp °C	ν_{max}, C=O	ν_{max}, NH	Methylene	Methyne	R_1	R_2
	Camphorimide	246–248	1690 (s) 1730 (s)	3080 (m) 3200 (m)	2.08 (4 H, m)	2.7 (1 H, m)		
IIIa	$R_1 = R_2 = H$	154–156	1665 (s) 1725 (m)	3240 (m) 3320 (m)	1.99 (4 H, m)	2.82 (1 H, m)	4.58 (1 H, s)	4.58 (1 H, s)
IIIb	$R_1 = COCH_3$; $R_2 = H$	82–83	1685 (s) 1695 (m)	3200 (m) 3420 (m) 3540 (m) 1575 (w) 1630 (m)	2.07 (4 H, m)	2.80 (1 H, m)	2.12 (3 H, s)	8.0 (1 H, d) $\Delta\nu$ = 17 Hz
IIIc	$R_1 = COPh$; $R_2 = H$	172 ± 0.5	1665 (s) 1705 (s) 1755 (m)	3240 (m) 1580 (w) 1600 (m)	2.08 (4 H, m)	2.80 (1 H, m)	7.70 (5 H, m)	8.50 (1 H, d) $\Delta\nu$ = 18 Hz
IIId	R_1 = *m*-$COC_6H_4CH_3$; $R_2 = H$	174–175	1660 (s) 1710 (s) 1755 (m)	3210 (m) 3290 (m) 1585 (m) 1605 (w)	2.13 (4 H, m)	2.83 (1 H, m)	2.36 (3 H, s) 7.65 (4 H, m)	8.75 (1 H, d) $\Delta\nu$ = 17 Hz
IIIe	$R_1 = CO_2C_2H_5$; $R_2 = H$	100 ± 0.5	1695 (s) 1730 (s) 1755 (m)	3300 (m)	2.08 (4 H, m)	2.85 (1 H, m)	1.30 (3 H, t) 4.28 (2 H, q) *J* = 7.2 Hz	8.48 (1 H, d) $\Delta\nu$ = 14 Hz
IIIf	$R_1 = COC_2H_5$; $R_2 = H$	70 ± 0.5	1700 (s) 1750 (s)	3200 (m) 1610 (w)	2.05 (4 H, m)	2.80 (1 H, m)	1.18 (3 H, t) 2.25 (2 H, q) *J* = 8 Hz	8.16 (1 H, d) $\Delta\nu$ = 10 Hz
IIIg	$R_1 = COCF_3$; $R_2 = H$	111–112	1660 (s) 1710 (s) 1760 (m)	3230 (w) 3280 (m) 1575 (m)	2.10 (4 H, m)	2.85 (1 H, m)		6.9 (broad signal)
IIIh	$R_1 = Ph$; $R_2 = H$	117–118	1680 (s) 1735 (m)	3310 (m) 1600 (m)	2.11 (4 H, m)	2.87 (1 H, m)	7.1 (5 H, m)	6.48 (1 H, s)
IIIi	R_1 = 2,4-$C_6H_3(NO_2)_2$; $R_2 = H$	246–248	1705 (s) 1745 (w)	3325 (m) 1600 (m) 1620 (m)	2.20 (4 H, m)	3.05 (1 H, m)	6.75 (1 H, d) 8.40 (1 H, q) 9.26 (1 H, d) *J* = 9, 3 Hz	9.70 (broad)
IIIj	$R_1 = R_2 = COCH_3$	115	1710 (s) 1730 (s) 1760 (m)		2.125 (4 H, m)	2.90 (1 H, m)	2.29 (3 H, s)	2.41 (3 H, s)
IIIk	$R_1 = Ph$; $R_2 = COCH_3$	106–107	1680 (s) 1700 (s) 1740 (m)		2.02 (4 H, m)	2.83 (1 H, m)	7.50 (5 H, m)	2.03 (3 H, s)
IIIl	$R_1 = R_2 = CH_2Ph$	151–152	1690 (s) 1740 (m)		1.37 (4 H, m)	2.48 (1 H, m)	4.28 (2 H, s)	4.44 (2 H, s)
IIIm	*N*,*N*′-Biscamphorimidyl	348–350	1700 (s)		2.16 (8 H, m)	2.83 (2 H, m)		

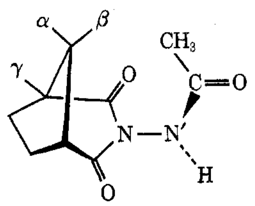
[a] Ir taken in Nujol medium. Abbreviations: s, strong; m, medium; and w, weak. [b] Nmr in $CDCl_3$ (30 mg in 0.3 ml) at 44.5° using TMS internal reference standard. Parentheses include proton count and the multiplicities are abbreviated as s, singlet; d, doublet; t, triplet,; q, quartet; and m, multiplet. Coupling constants and internal chemical shifts in hertz are indicated.

singlets for the acetyl methyl groups ($\Delta\nu$ = 7 Hz in $CDCl_3$) are observed. A singlet observed for the acetyl methyl protons (Figure 1) in IIIb eliminates the possibility of hindered rotation about the N–N′ bond.

A slow rotation about the N′–CO bond provides two different magnetic environments for the β-methyl: (i) deshielded as in IV and (ii) shielded as in V.[3] Under these conditions, the different magnetic environments experienced by the β-methyl in the two conformations IV and V are very nearly like those of the γ- and α-methyls, respectively. In the case of IIIg, the substituent $-COCF_3$ provides slightly different shielding and deshielding effects on the β-methyl, and, as a result, the latter is not allowed to become magnetically equivalent to either of the two methyls (Table I).



IV



V

With slow rotation about the N′–CO bond, one might expect two different signals for the acetyl methyl protons corresponding to IV and V. However, as the shielding and deshielding effects on the acetyl methyl group due to the β-methyl and the carbonyls of the cage moiety are averaged out by a fast rotation about the N–N′ bond, a sharp singlet is observed for the acetyl methyl in IIIb (Figure 1).

The nmr spectra of these compounds are temperature dependent. The three methyl groups of IIIb appear as a set of four signals in nitrobenzene (Figure 2). The β-methyl signals of practically equal intensity (1.5 H), separated by 19 Hz at 44.5°, coalesce to a singlet at 70° and the three methyl groups appear as three sharp signals at higher temperatures. Free-energy barriers to

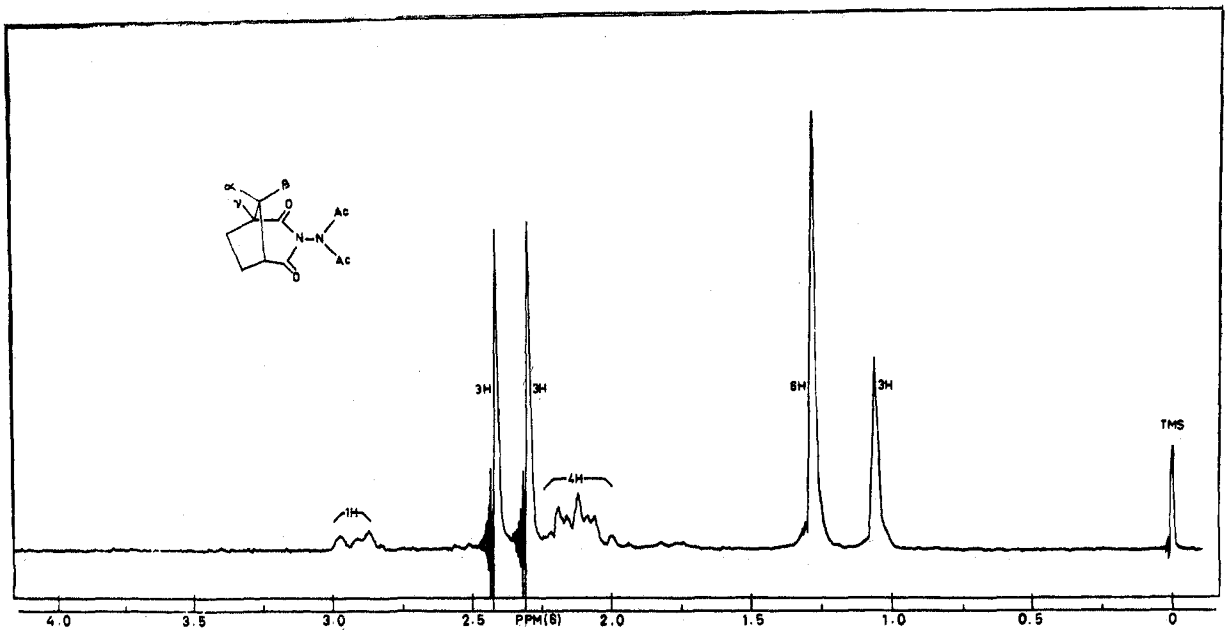


Figure 3.—60-MHz nmr spectrum of *N′,N′*-diacetyl-*N*-aminocamphorimide (IIIj) in $CDCl_3$ at 44.5°.

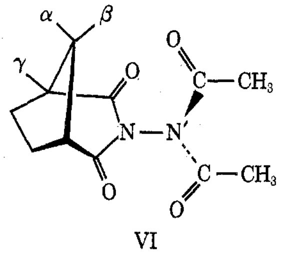
rotation about the N′–CO bond for the compound IIIb, calculated from the temperature-dependent methyl signals, $\Delta G_{70}^{\ddagger}$, was found to be 17.7 kcal/mol. This is in fair agreement with $\Delta G^{\ddagger}$ values reported for the N–CO hindered rotation in urethanes[2] and other systems.[1]

***N′*-Disubstituted *N*-Aminocamphorimides.**—The nmr spectra of the disubstituted *N*-aminocamphorimides indicate the possibility of slow rotation about the N–N′ bond. Conformational studies by nmr spectroscopy about the N–N single bonds are complicated by the possibility of partial double bond formation and the inversion at the trivalent nitrogen besides steric and nonbonding repulsive interactions. Tetra- and hexahydropyridazine systems[1] are further complicated by a ring inversion process. The present system is much simplified and provides unambiguous assignments for the spectral changes. The cage moiety, *i.e.*, the bicyclic camphorimidyl system, provides no scope for the ring inversion process. The possibility of inversion at the nitrogen, in the planar imide ring and also at the exocyclic nitrogen when attached to an acyl group, is eliminated. The "cage moiety" with a nonplanar structure provides a suitable basis for the study of the magnetic environment of N′ substituents.

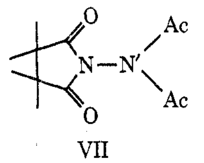
***N′,N′*-Diacyl-*N*-aminocamphorimide (IIIj).**—The three methyl groups (α, β, and γ) of the camphorimidyl system appear as two signals of 3 H (δ 1.05) and 6 H (1.30) and the acetyl groups as two singlets, each of 3 H intensity with an internal chemical shift of 7 Hz in $CDCl_3$ (Figure 3). The chemical shift of other protons (methylene and methyne) are recorded in Table II.

Preferred conformations about the N–N′ bond in tetraacylhydrazines[4] of type II have been rationalized through nmr studies in terms of nonbonded repulsions between the acyl substituents in the planar transition state; the two acyl groups attached to the exocyclic nitrogen atom would lie above and below the plane of the succinimidyl ring. X-Ray analysis of *N,N′*-bisuccinimidyl[9] shows that the two ring planes make a dihedral angle of 65°. Free-energy barriers to rotation about the N–N′ bonds estimated from the variable-temperature spectral measurements have been reported to be in excess of 18–20 kcal/mol.[3]

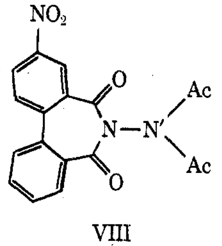
In the compound IIIj, the restricted rotation about the N–N′ bond seems to be responsible for orienting the two acetyl groups, one above and one below the common plane of the imide bridge, leading to a magnetic nonequivalence as represented in VI. Molecular models show that in the noncoplanar conformation (VI) the two acetyl groups experience different magnetic environments due to the "cage moiety." In the absence of this property, compounds VII[4] and VIII[10] do not show different signals for the acetyl groups. A fixed noncoplanar conformation VI also allows for the magnetic equivalence of one of the *gem*-methyl groups (β-methyl, syn to the N–N′ bond) with that of the angular γ-methyl.



VI



VII



VIII

Variable-temperature spectral measurements of the compound in DMSO-d_6 show that acetyl signals move closer as the temperature is raised accompanied by a broadening of signals at 150° ($\Delta\nu_{30°} = 15$ Hz and $\Delta\nu_{150°}$

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(9) G. S. D. King, *J. Chem. Soc. B*, 1224 (1966).

(10) N. V. Riggs and S. M. Verma, *Aust. J. Chem.*, **23**, 1913 (1970).

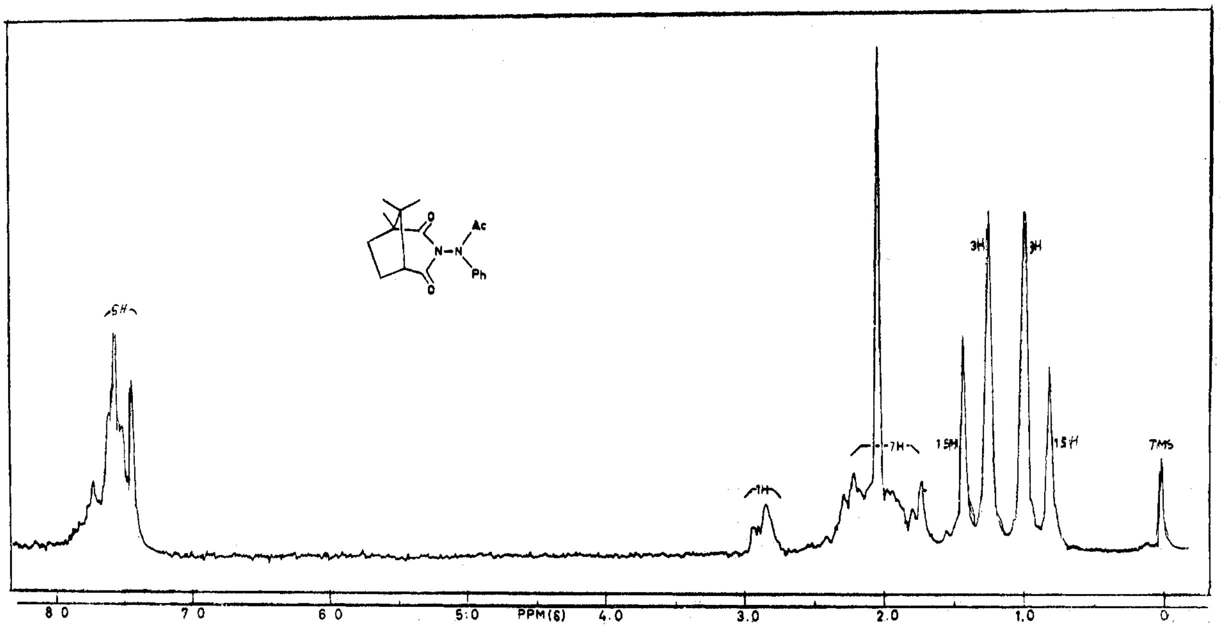
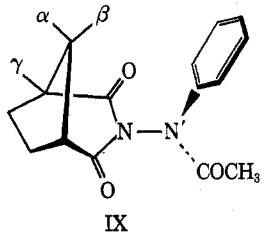


Figure 4.—60-MHz nmr spectrum of *N*′-acetyl-*N*-anilinocamphorimide (IIIk) in $CDCl_3$ at 44.5°.

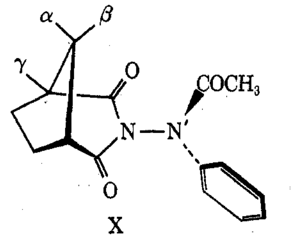
= 8.8 Hz). The exact coalescence temperature, T_c, could not be determined due to the experimental limitations but one would expect that coalescence would not occur for at least another 30°. $\Delta G^{\ddagger}$ calculated on the basis of spectral analysis corresponds to 23.2 and 23.9 kcal/mol, respectively, for T_c = 170 and 180°.

***N*′-Acetyl-*N*-anilinocamphorimide (IIIk).**—The nmr spectrum of the compound (Figure 4) in $CDCl_3$ shows a sharp singlet (3 H) for the acetyl group and a set of four signals for the three methyl groups of the camphorimidyl along with multiplets for the methylene, methyne, and aromatic protons. Appearance of two signals for the β-methyl, each of 1.5 H (at δ 0.8 and 1.43), provides evidence for the two different conformations of the compound. The shielding constant for the α-methyl (3 H singlet at δ 0.99) is not affected by the substituents at exocyclic nitrogen, while that of γ-methyl shows splitting at δ 1.23 (Figure 4).

As in tetraacyl compounds and IIIj, two different conformations for the compound IIIk are possible due to restricted rotation about the N-N′ bond, which could be represented as IX and X. The shielding and deshielding effects on β-methyl due to phenyl and acetyl groups, respectively, are indicated by the spectrum (Figure 4). In one of the conformations (IX), where the β-methyl is facing the phenyl group, a shielding effect is observed (δ 0.8) as compared to that in camphorimide, δ 1.05 (Table I). In the other preferred conformation (X), the acetyl group lies syn to the β-methyl, causing a deshielding effect (δ 1.43). From the proton intensity measurements of these signals, the two conformations appear in equal population in CDCl solution at 44.5°.



IX



X

The spectrum of the compound IIIk in nitrobenzene, however, gives a slightly different picture. The two signals for the acetyl methyl group in the two conformations, which accidentally overlapped in $CDCl_3$, are observed with an internal chemical shift of 2 Hz. The proton intensities of the upfield and low-field signals are in the ratio of 3:4. Similarly, the proton intensity ratio of the two signals of the β-methyl is also changed from 1:1 to 3:4. Variable-temperature spectral measurements in nitrobenzene have shown that the signals due to the β-methyl and acetyl methyl, separated by 41 and 2 Hz, respectively, move closer when the temperature is raised, the values being 37 and 1.2 Hz at 100°. Based on the separation of the acetyl signals at 44.5 and 100°, a free energy of activation not less than 21 kcal/mol could be obtained.

***N*′,*N*′-Dibenzyl-*N*-aminocamphorimide (IIIl).**—In the nmr spectrum of the compound IIIl in $CDCl_3$ (Figure 5), the three methyl signals appear to be shielded by δ 0.2–0.3 as compared to that of camphorimide; in addition the ring methylene protons are also shielded. The four exocyclic benzylic methylene protons appear as two sharp singlets of equal intensity with an internal chemical shift of 9.5 Hz.

The absence of AB quartets for the geminal benzylic protons rules out the possibility of slow inversion at the exocyclic nitrogen atom[11] and that the degree of nonequivalence due to asymmetry of the cage moiety[12] is immeasurably small. Therefore the two singlets for benzylic protons in the nmr spectrum can easily be explained on the basis of a slow rotation about the N-N′ bond. For compounds XI[13] and XII,[14] one should not expect AB quartets for the geminal benzylic protons due to the symmetry properties of the molecules, but two singlets might have been expected. Compounds

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[11] M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, **No. 5**, 339 (1970).

[12] R. E. Lyle and J. J. Thomas, *ibid.*, **No. 11**, 897 (1969).

[13] N. V. Riggs and S. M. Verma, unpublished results.

[14] S. M. Verma and C. Koteswara Rao, *Tetrahedron*, **28**, 5029 (1972).

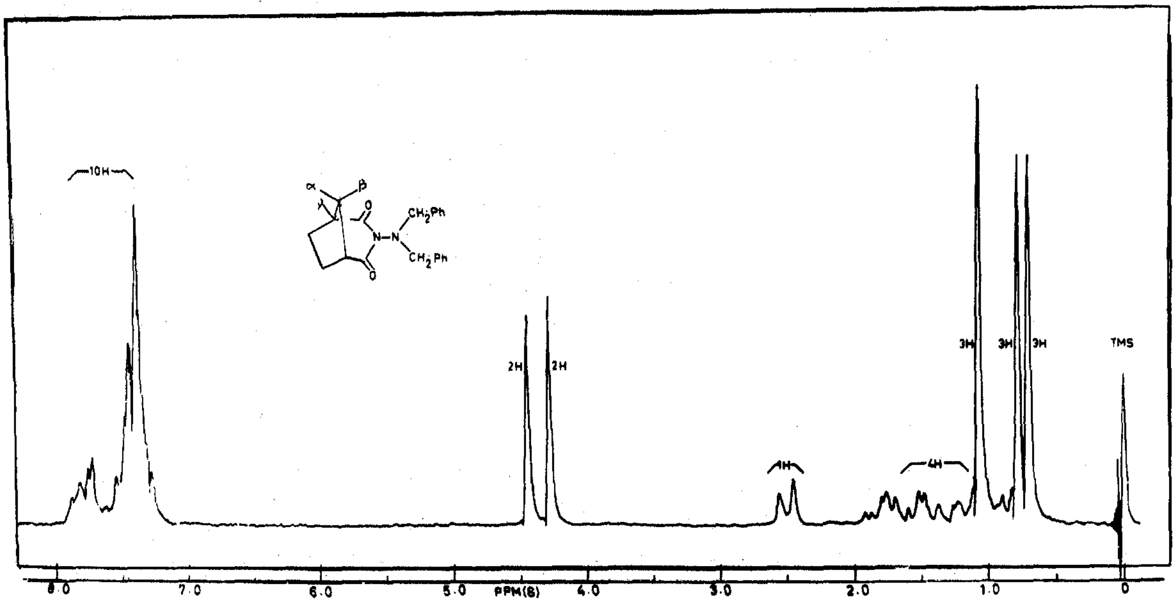
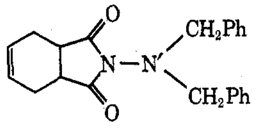
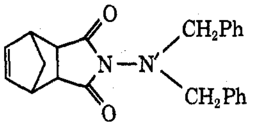


Figure 5.—60-MHz nmr spectrum of *N*′,*N*′-dibenzyl-*N*-aminocamphorimide (IIIl) in $CDCl_3$ at 44.5°.

XI and XII show only sharp singlets of 4 H intensities, which may be attributed to the imidyl system being far away from the cage moiety. On the other hand, in IIIl, the imidyl system forms a part of the cage moiety leading to steric factors which play a significant role in hindering the N–N′ bond rotation at room temperature.



XI

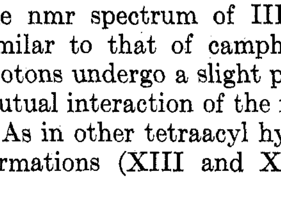


XII

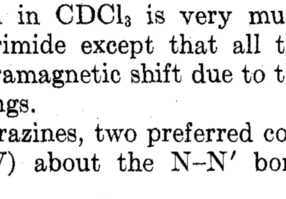
Variable-temperature spectral measurements in nitrobenzene show that the benzylic methylene signals, which are separated by 11.8 Hz at 44.5°, coalesce at 100°. $\Delta G^{\ddagger}$ calculated from $\Delta\nu$ and T_c values is found to be 19.7 kcal/mol, which is in good agreement with the values reported by Fletcher and Sutherland[15] for the *N*,*N*-diacyl-*N*′,*N*′-dibenzylhydrazine system ($\Delta G^{\ddagger}$ = 19.6 ± 0.5 kcal/mol).

***N*,*N*′-Biscamphorimidyl (IIIm).**—The appearance of the nmr spectrum of IIIm in $CDCl_3$ is very much similar to that of camphorimide except that all the protons undergo a slight paramagnetic shift due to the mutual interaction of the rings.

As in other tetraacyl hydrazines, two preferred conformations (XIII and XIV) about the N–N′ bond could be expected. In XIII, all the chemically equivalent protons of the ring A and ring B are magnetically equivalent. Similarly, in XIV, the chemically equivalent protons of ring A′ and ring B′ are magnetically equivalent. Molecular models show that the magnetically equivalent protons of XIII are not equivalent to those in the other conformation, XIV. For example, the angular γ-methyls in XIII are facing the *gem*-methyls of the opposite rings, whereas in XIV the γ-methyls are facing the methylene bridges of the opposite rings. A complicated spectrum, thus, might have been expected, but the observed spectrum is simple (three sharp signals for the six methyls, each of 6 H intensity). This is probably because the difference in magnetic environments of the protons in the two conformations is insufficient to resolve the peaks. In nitrobenzene, however, the most downfield methyl signal, probably that of γ-methyl, appears broad due to "solvent shifts" supporting the above argument.



XIII



XIV

Studies on N′-substituted *N*-aminocamphorimides have indicated that the N′-monoacyl derivatives tend to show a partial double bond character about the N′-CO bond; $\Delta G^{\ddagger}$ is of the order of 18 kcal/mol. *N*′,*N*′-Diacyl derivatives prefer a noneclipsed conformation about the N–N′ bond and the high torsional barriers could be due to repulsive interactions between the carbonyls at the two nitrogens. In case of bulky substituents, *e.g.*, *N*′,*N*′-dibenzyl derivatives, steric factors could be responsible for the hindered rotation about the N–N′ bond.

Experimental Section

Preparation of Compounds.—Camphorimide,[16] *N*-aminocamphorimide (IIIa),[17] *N*-anilinocamphorimides (IIIh and IIIi),[18] and *N*′-acetyl-*N*-anilinocamphorimide (IIIk)[19] were prepared according to the methods already reported.

***N*′-Monoacyl derivatives (IIIb–IIIg)** were obtained by acylation of the *N*-amino compound (IIIa) with acyl chlorides (in equimolecular proportions) in the presence of pyridine at room temperature. Elemental analyses of the compounds were in good agreement with the calculated values. The melting points of the compounds are recorded in Table II.

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(15) J. R. Fletcher and I. O. Sutherland, *J. Chem. Soc. D*, No. 13, 706 (1969).

(16) W. C. Evans, *J. Chem. Soc.*, **97**, 2237 (1910).

(17) V. Alexa and G. Gheorghin, *Bull. Soc. Chim. Fr.*, **49**, 1112 (1931).

(18) Chaplin, *Ber.*, **25**, 2566 (1892); Beilstein's Handbuch Band XXI, 420.

(19) Chaplin, *Ber.*, **25**, 2567 (1892); Beilstein's Handbuch Band XXI, 421.

***N′,N′*-Diacetyl-*N*-aminocamphorimide** (**IIIj**) was obtained by refluxing *N*-aminocamphorimide (IIIa) with acetic anhydride for about 2 hr, the excess of the latter being removed off under reduced pressure and the product being recrystallized from ethanol, mp 115°.

Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 60.00; H, 7.14. Found: C, 59.73; H, 7.49.

***N′,N′*-Dibenzyl-*N*-aminocamphorimide** (**IIIl**) was obtained by heating *N*-aminocamphorimide with 2 mol of benzyl chloride in the presence of pyridine at 120° for about 2 hr. The excess of benzyl chloride and pyridine were removed off under reduced pressure and the product was recrystallized from ethanol, mp 152°.

Anal. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.59; H, 7.44. Found: C, 76.81; H, 7.62.

***N,N′*-Biscamphorimidyl** (**IIIm**) was obtained by heating a mixture of 2 mol of camphoric anhydride and 1 mol of hydrazine hydrate at 240–250° for 3–4 hr. It was recrystallized from hot ethanol, mp 350°.

Anal. Calcd for $C_{20}H_{28}N_2O_4$: C, 66.66; H, 7.77; mol. wt, 360. Found: C, 66.27; H, 7.83; mol wt, 362. The molecular weight of the sample was determined by an osmometer (Mechrolab Model 301 A).

The nmr spectra were recorded on a Varian A-60D spectrometer equipped with a variable-temperature controller Model V-6040. Ir spectra were recorded in Nujol on Perkin-Elmer spectrophotometers (Model 621 and 257). Ir and nmr data (excluding chemical shifts of the methyl groups listed in Table I) and the melting points are recorded in Table II.

Registry No.—IIIa, 37710-30-8; IIIb, 37710-31-9; IIIc, 37710-32-0; IIId, 37710-33-1; IIIe, 37710-34-2; IIIf, 37710-35-3; IIIg, 37710-36-4; IIIh, 37710-37-5; IIIi, 37780-36-2; IIIj, 37710-38-6; IIIk, 37710-40-0; IIIl, 37710-39-7; IIIm, 37710-41-1; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; *m*-toluoyl chloride, 1711-06-4; ethyl chloroformate, 541-41-3; propionyl chloride, 79-03-8; trifluoroacetyl chloride, 354-32-5; acetic anhydride, 108-24-7; benzyl chloride, 100-44-7; camphoric anhydride, 76-32-4.

Acknowledgment.—Thanks are due to Professor G. B. Singh for his keen interest and to Professor N. V. Riggs, University of New England, Australia, for recording a variable-temperature spectra of the compound IIIj.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Tetramethylenehalonium Ions

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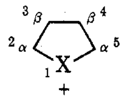
Received August 16, 1972

Carbon-13 nmr chemical shifts for the cyclic five-membered halonium ions and their precursors have been tabulated. Consistent downfield shifts of 30–35 ppm have been observed for the halo-substituted carbon (α carbon) in going from precursor to ion when the α carbon is primary. Addition of a methyl group to the α carbon of a substituted ion causes a 35-ppm downfield shift. The coupling constants for these ions have also been tabulated. A 10–15-Hz increase in the *J* values of the α carbons of halonium ions, compared to *J* values for precursors, was observed. These data suggest that highly electronegative heteroatoms give carbonium ion character to the attached carbons.

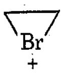
Since the preparation of the stable five-membered tetramethylenehalonium ions[2] **1** their reactions with various nucleophiles have been studied.[3] In the case of the tetramethylenechloronium ion, rate studies[4] with various carboxylic acids in SO_2 at −65° gave rate constants which were significant as possible measures of the nucleophilicities of the carboxylic acids.



1

We have recently prepared halonuum ions with alkyl or halo substituents at the 3 position of the ring and have studied the direction of ring opening by a variety of nucleophiles. The relative percentages of products formed appeared to be affected by the inductive and steric effect of the ring substituent and the nucleophilicity of the nucleophile.[5]

Olah and White have correlated the charge density on various carbons of positively charged species with the ^{13}C chemical shift.[6a] Among the species investigated were the ethylenebromonium (**2**) and tetramethylethylenebromonium (**3**) ions. Reported chemical shifts of the ring carbons were 120.8 and 55.2 ppm, respectively, upfield from CS_2.[6a,7] It was shown that ^{13}C chemical shifts offer a possibility of distinguishing open chain, equilibrating, and bridged cationic species.[6]



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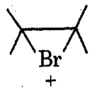
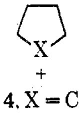
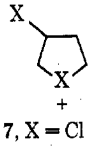


3

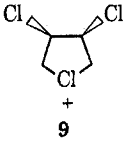
We now wish to report ^{13}C nmr data (δ_{CS_2} and J_{CH}) for the five-membered halonium ions **4–13** and their precursors (Table I). Our study provides an illustration of the applicability of presently available instru-



4, X = Cl
5, X = Br
6, X = I



7, X = Cl
8, X = Br



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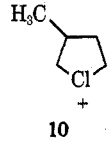

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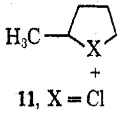

11, X = Cl
12, X = Br
13, X = I

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(1) Postdoctoral Investigator.

(2) G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968).

(3) P. E. Peterson, P. R. Clifford, and F. J. Slama, *ibid.*, **92**, 2840 (1970).

(4) P. E. Peterson and F. J. Waller, *ibid.*, **94**, 991 (1972).

(5) P. E. Peterson and B. R. Bonazza, *ibid.*, **94**, 5017 (1972).

(6) (a) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969), and references cited therein; (b) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

(7) G. A. Olah and R. D. Porter, *ibid.*, **93**, 6877 (1971).