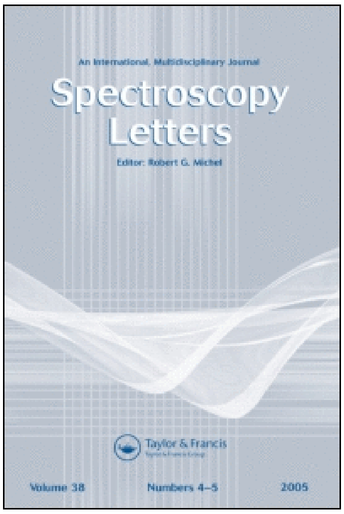


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The 25.16 MHz Carbon-13 Magnetic Resonance Spectra of a Tricyclic Acetal and a Tricyclic Hemiacetal

A. Harry Andrist[a]; Mark J. Kovelan[a]
[a] Department of Chemistry, The Cleveland State University, Cleveland, Ohio

To cite this Article Andrist, A. Harry and Kovelan, Mark J.(1977) 'The 25.16 MHz Carbon-13 Magnetic Resonance Spectra of a Tricyclic Acetal and a Tricyclic Hemiacetal', Spectroscopy Letters, 10: 3, 127 — 132
To link to this Article: DOI: 10.1080/00387017708067503
URL: http://dx.doi.org/10.1080/00387017708067503

SPECTROSCOPY LETTERS, 10(3), 127-132 (1977)

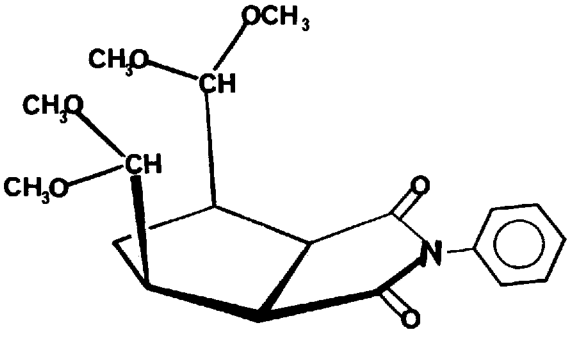
THE 25.16 MHz CARBON-13 MAGNETIC RESONANCE SPECTRA OF A TRICYCLIC ACETAL AND A TRICYCLIC HEMIACETAL

Key Words: Acetal Methanolysis, Cmr Spectrum

A. Harry Andrist* and Mark J. Kovelan

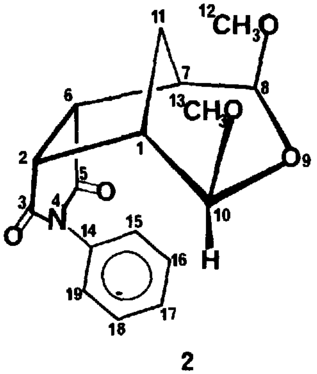
Department of Chemistry
The Cleveland State University
Cleveland, Ohio 44115

Ozonolysis of the N-phenylmaleimide-cyclopentadiene Diels-Alder adduct in methanol followed by reductive work-up with dimethyl sulfide affords 3-phenyl-endo,endo,cis-6,8-bis(dimethoxymethyl)-3-azabicyclo[3.3.0]octan-2,4-dione (1), mp 105.5-107°.[1]

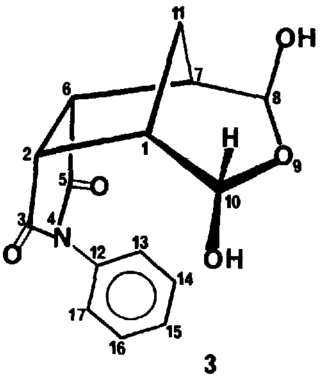


1

We have observed that heating acetal **1** in aqueous acidic methanol produces two new compounds: a soluble compound (2), mp 180-184°, which crystallizes as colorless plates upon cooling, and an insoluble compound (**3**). mp 204-206°. The structures of the new compounds have now been assigned from their 25.16 MHz natural abundance carbon-13 magnetic resonance (cmr) spectra and ancillary spectral data[2,3] as the tricyclic acetal, *cis*, *endo*-4-phenyl-4-aza-9-oxa-8,10-*cis*,*exo*-dimethoxytricyclo[$5.3.1.0^{2,6}$] undecan-3,5-dione (**2**), and the tricyclic hemiacetal, *cis*,*endo*-4-phenyl-4-aza-9-oxa-8,10-*trans*-dihydroxytricyclo--[$5.3.1.0^{2,6}$] undecan-3,5-dione (**3**).



2



3

The infrared spectrum of the insoluble compound (**3**) shows the presence of the hydroxyl group ($\bar{\nu}_{OH}(CH_3CN)$ @ 3635-3540 cm^{-1}), and this is confirmed by its isobutane chemical ionization mass spectrum which exhibits $[M + H - H_2O]^+$ @

m/e 272. Similary, isobutane chemical ionization of 2 confirms the presence of a methoxy group with $[M + H - CH_3OH]^+$ @ m/e 286.

The 25.16 MHz cmr spectra of 2 (Table I) and 3 (Table II) conclusively demonstrate the presence of a molecular plane of symmetry in 2 and the absence of one in compound 3: Acetal 2 exhibits only one carbonyl carbon at 176.3 ppm from internal tetramethylsilane, while hemiacetal 3 has two at 174.4 and 171.6 ppm. All three remain as singlets in the single frequency off-resonance decoupled cmr spectra. The methoxy carbons of acetal 2 are magnetically equivalent and appear at 56.2 ppm with $J_{^{13}C-^{1}H}$ = 140 Hz as in dimethyl ether.[4,5] The cis,exo configuration of the methoxy groups in 2 is differentiated from the cis,endo configuration on the basis of the observed cmr chemical shifts. Sterically compressed groups are well-known to exhibit deshielded proton chemical shifts and shielded carbon chemical shifts (relative to unstrained models).[4,5] Using acetal 1 and related imide-acetals[1] as unstrained models one finds that the methoxy carbons all occur within the chemical shift range of 54.9 ± 1.0 ppm from internal tetramethylsilane. The magnetically equivalent methoxy carbons for acetal 2 are 1.3 ppm downfield of this mean, which suggests that compound 2 experiences even less steric compression than does any one of the model compounds. This conclusion is consistent with structure 2 based on an examination of molecular models.

Hemiacetal 3 contains no methoxy carbons, but a comparison of the chemical shifts of the methine carbons bonded to two oxygen atoms in 2 and 3 is instructive. These carbons occur at 89.3 and 102.2 ppm for hemiacetal 3 (doublet, $J_{^{13}C-^{1}H}$ = 180 and 185 Hz, respectively) and at 99.8 ppm for acetal 2 (doublet, $J_{^{13}C-^{1}H}$ = 170 Hz). These cmr chemical shift data indicate that hemiacetal 3 contains one sterically compressed and one relatively uncompressed methine carbon while acetal 2 must possess one methine carbon bonded to two oxygens which experiences intermediate steric compression, relative to the two in hemiacetal 3. Both conclusions are consistent with the proposed structures and their respective molecular models.

These two simple examples dramatically illustrate the utility of natural abundance cmr spectroscopy in structural elucidations, especially for polycyclic heteroatomic systems. In these two instances, the cmr spectrum was the most important single piece of spectral evidence obtained.

TABLE I

Cmr Spectrum of *cis,endo*-4-phenyl-4-aza-9-oxa-8,10 *cis*, *exo*-dimethoxytricyclo $[5.3.1.0^{2,6}]$ undecan-3,5-dione (2)

Chemical Shift[a]	Multiplicity[b]	$J_{^{13}C-H}$, Hz[c]	Assignment
27.9	t	135	C-11
40.8	d	140	C-1,7
46.8	d	140	C-2,6
56.2	q	140	C-12,13
99.8	d	170	C-8, 10
123.5	s	--	C-14
127.0	d	160	C-17
128.8	d	160	C-16,18
129.2	d	165	C-15,19
176.3	s	--	C-3,5

[a] Values reported in ppm from internal tetramethylsilane.

[b] From the single frequency off-resonance decoupled spectrum obtained at 46401 Hz.

[c] Coupling constants are reported only for those protons directly bonded to the observed carbon from the gyro-gated spectrum.

TABLE II

Cmr Spectrum of *cis*,*endo*-4-phenyl-4-aza-9-oxa-8,10-*cis*, *trans*-dihydroxytricyclo $[5.3.1.0^{2,6}]$undecan- 3,5-dione (3)

Chemical Shift[a]	Multiplicity[b]	$J_{^{13}C-H}$,Hz[c]	Assignment
25.2	t	135	C-11
39.9	d	135	C-2
42.8	d	135	C-6
45.3	d	140	C-1
48.0	d	140	C-7
89.3	d	180	C-8
102.2	d	185	C-10
122.7	d	160	C-15
125.7	d	160	C-14,16
128.7	d	165	C-13,17
137.3	s	--	C-12
171.6	s	--	C-3
174.4	s	--	C-5

[a] Values reported in ppm from internal tetramethylsilane.

[b] From the single frequency off-resonance decoupled spectrum obtained at 46401 Hz.

[c] Coupling constants are reported only for those protons directly bonded to the observed carbon from the gyro-gated spectrum.

ACKNOWLEDGEMENTS

The use of the Varian XL-100 Fourier Transform Nmr Spectrometer at the Major Analytical Instruments Facility of Case Western Reserve Univeristy and the financial assistance of a Cleveland State University Research Initiation Award are acknowledged with thanks.

REFERENCES AND NOTES

1. A. H. Andrist and M. J. Kovelan, *Spectrosc. Lett.*, **8**, 719-729 (1975).

2. For **2**: ir ($CHCl_3$) $\bar{\nu}_{CH}$ @ 3020-2840 cm^{-1}, $\bar{\nu}_{C=O}$ @ 1710, $\bar{\nu}_{C=C}$ @ 1600, and $\bar{\nu}_{OCO}$ @ 1110; ms (isobutane chemical ionization) $[M + H]^+$ @ *m/e* 318 and $[M + H - CH_3OH]^+$ @ 286; PMR ($CDCl_3$, 60 MHz) δ_{TMS} 7.30 (aromatic, *m*, 5H), 4.60 (methine, *m*, 2H), 3.43 (methoxy, *s*, 6H), 2.77 (methine, *m*, 4H), and 1.60 (methylene, *m*, 2H). For **3**: ir (CH_3CN) $\bar{\nu}_{OH}$ @ 3635-3540 cm^{-1} and $\bar{\nu}_{C=O}$ @ 1810 and 1735; ms (isobutane chemical ionization) $[M + H - H_2O]^+$ @ *m/e* 272; PMR ($CDCl_3$, 60 MHz) δ_{TMS} 7.30 (aromatic, *m*, 5H), 5.77 (hemiacetal methine, *d*, J = 5Hz, 1H), 5.52 (hemiacetal methine, *d*, J = 5Hz, 1H), 3.2 (methine plus hydroxyl, *m*, 6H), and 1.90 (methylene, *m*, 2H).

3. Both new compounds afforded satisfactory elemental analyses: **2**: *Anal.* Calcd. for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.14; H, 5.79; N, 4.36. **3**. *Anal.* Calcd. for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Calcd. for $C_{15}H_{15}NO_5$-H_2O: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.70; H, 4.88; N, 5.20.

4. J. B. Strothers, "Carbon-13 Nmr Spectroscopy," Academic Press, New York, 1972.

5. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, 1972.

Received: 1-6-77
Accepted: 1-19-77