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Orientation of the Nitrogen Lone-Pair Electrons in Cannivonine

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Received November 5, 1975

The structure of cannivonine b (1) has been reasonably established using ^{1}H NMR spectra recorded in the presence of shift reagents.[1–3] The cannivonine b is a tricyclic alkaloid having a 1-cyclohexen-3-ol ring fixed on the azabicyclo[2.2.2]octane skeleton. Such a tricyclic compound can undergo syn–anti equilibration (Scheme I).

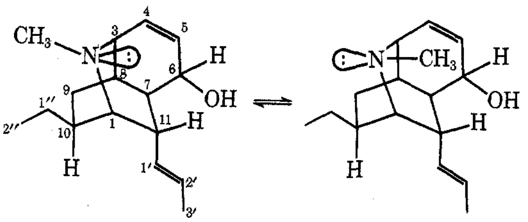
In the presence of the shift reagents, syn oriented nitrogen lone-pair electrons contribute to the formation of the eight-coordinate two donor atoms complex that involves O and N.[3] Recently Morishima and Yoshikawa[4] have found that the nitrogen lone pair of *N*-methyl-2-azabicyclo[2.2.2]oct-5-ene (and its dihydro derivative) is oriented in an anti position.

Table I. Ni(acac)$_2$ Induced ^{13}C Contact Shifts for 1 [a]

C	δ_C	Relative induced shift
1	52.17	+1.00
NCH_3	43.81	+1.62
3	56.24	+1.40
4	129.73	−0.52
5	131.34	−0.44
6	65.51	+0.84
7	25.40	+0.40
8	26.87	−0.33
9	25.65	+0.02
10	24.92	−1.38
11	25.17	−0.41
1′	130.71	+0.08
2′	121.37	−0.17
3′	13.41	+0.14
1″	25.02	+0.08
2″	12.10	0.00

[a] Identification from off-resonance ^{1}H; see Experimental Section for details of calculations.

Scheme I



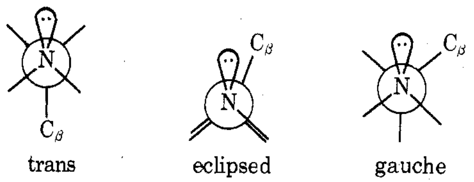
syn-1 *anti*-1

The NMR spectra, ^{1}H and ^{13}C, recorded in the presence of nickel bisacetylacetonate do not show the orientation of the metal relative to the double bond. The CNDO–MO calculations, carried out by the same authors, confirmed the preferential anti position of the nitrogen lone pair.[5,6] However, for cannivonine b, acetylacetonate can easily lie between the nitrogen and oxygen atoms and force the nitrogen lone pair into syn orientation (endo using Morishima nomenclature).

The syn orientation of the nitrogen lone pair is deduced from the ^{13}C NMR spectra of cannivonine (Table I).

The acetylacetonate relative induced shift of β carbons, with respect to the lone pair, is bigger if the lone pair is oriented trans (anti-coplanar) to this carbon. However, the gauche or eclipsed orientation shows a rather small contact shift (Scheme II). There are four carbons atoms β to the nitrogen lone pair (C-4, C-8, C-10, and C-11) and two β to the oxygen lone pairs (C-5 and C-7). Thus, the large C-10 relative induced shift of −1.38 is now understandable compared with the C-11, C-8, or C-4 induced shifts.

Scheme II



trans anti-coplanar eclipsed gauche

The oxygen atom has lone pairs oriented in such a manner that at the same time they are trans and eclipsed to C-5 and C-7. As a result, an average (~0.4) relative induced shift is observed.[7]

Finally, examination of steric repulsion in the 1-syn and 1-anti conformers shows that the syn conformers is effectively more stable. The interaction of 10-ethyl–NCH_3 and H-9β–NCH_3 in the syn conformer is smaller than the total interac-

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tion of the cyclohexene part–NCH_3 in the anti conformer. Since the lone pair electrons of the nitrogen atom have such an important effect on the β carbon situated in the anti-coplanar position, this effect could be used in the investigation by C-13 spectroscopy of the preferential orientation of the nonbonded electrons in different cyclic amines.

Experimental Section

The cannivonine b (1) sample was isolated as previously described.[1] Nickel bisacetylacetonate (Aldrich Chemical Co.) was dried under reduced pressure for 24 h at the temperature of boiling acetone. The ^{13}C NMR spectra were obtained on Brucker HF-X-10 and Jeolco FT spectrometers (22.6 and 25.1 MHz, respectively) with an internal lock ^2H. The δ_C were measured in parts per million using Me_4Si as a standard. Solutions of 1 (10.0%) in $CDCl_3$ in standard tubes (10 mm or 8 mm) at a temperature of 25 ± 1 °C were used. The $Ni(acac)_2$ relative induced shifts for all carbons were measured from the slopes of linear plots of observed ^{13}C contact shifts vs. concentration of acetylacetonate (induced ^{13}C contact shifts in hertz plotted vs. concentration of $Ni(acac)_2$ expressed in millimoles). The "true" shift of 2.20 ppm was observed for 0.025 mol of $Ni(acac)_2$ for C-1 and was normalized to unity.

Acknowledgment. The author thanks the National Research Council of Canada for a small research grant.

Registry No.—1, 52340-94-0.

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Configuration of the Photoisomers of Benzylideneanilines

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Received February 26, 1976

Benzylideneanilines (ArCH=NAr′) are formally related to stilbenes (ArCH=CHAr′) and azobenzenes (ArN=NAr′), but are different from the latter two in the respect that *Z* (cis) and *E* (trans) isomers have not been isolated. It was reported that the irradiation of a solution of benzylideneaniline at low temperature converts it reversibly to a photoisomer of different uv absorption,[1a] but no concrete evidence as to its structure has been presented although a *Z* structure has been assigned to the photoisomer of 4,4′-dichlorobenzylideneaniline on the basis of dipole moment measurements.[2]

We have determined the uv spectra of photoisomers of many substituted benzylideneanilines in an EPA matrix (ether–isopentane–ethanol) at −196 °C and showed that the imino arene ring of the photoisomer is about 90° rotated from the ArCH=N– plane around the N–Ar′ bond.[3] However, it was not possible to determine whether or not the photoisomer has a *Z* structure.

As described in our previous paper,[3] the photoisomers are stable in a matrix at −196 °C for a long period and stable for several hours in solutions (EPA, methylcyclohexane, or acetone) at −72 °C. Therefore, the configuration of the photoisomers was studied by determining ^1H NMR spectra in acetone-d_6. Since this photoisomerization is complete only in dilute concentrations (~10^{-3} M), spectra were determined by use of a Fourier transform instrument (accumulation, 500–1000 sweeps). When the photoisomers produced at −196 or −72 °C were warmed to room temperature, the ^1H NMR and uv spectra showed that the photoisomers were completely converted back to the original *E* isomers. This change can be reproduced many times.

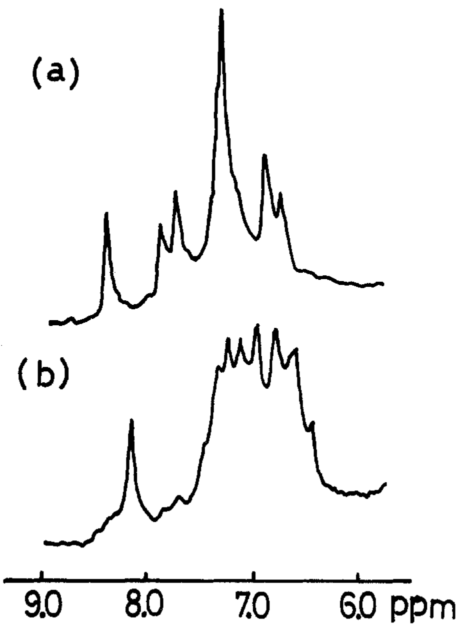
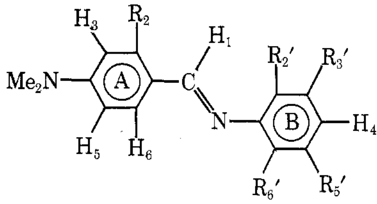


Figure 1. NMR spectra of (a) 1 and (b) its photoisomer **1a.**

p-Dimethylaminobenzylideneaniline (1) and its methyl derivatives were chosen for our study because they have strong absorption maxima at wavelengths greater than 300 nm, and are almost completely converted to their photoisomers upon irradiation in acetone-d_6 solutions with a high-pressure mercury lamp. In order to ascertain the assignments of aromatic NMR absorptions, some derivatives of 1 deuterated at suitable positions were synthesized and their spectra were determined.

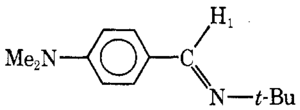


1, $R_2 = R_2' = R_3' = R_5' = R_6' = H$

2, $R_2' = R_6' = Me; R_2 = R_3' = R_5' = H$

4, $R_2 = R_2' = R_6' = H; R_3' = R_5' = Me$

5, $R_2 = Me; R_2' = R_3' = R_5' = R_6' = H$



3

Results and Discussion

Figure 1a is the NMR spectrum of 1 in acetone-d_6 at −75 °C; H_1 (s, 8.41 ppm from internal Me_4Si); H_2 and H_6 (q, 7.85 ppm); H_3 and H_5 (q, 6.84 ppm); other ArH (m, ca. 7.4 ppm). Figure 1b is the NMR spectrum of the photoisomer of 1 (**1a**),