4-Butyl-1,2-diphenylpyrazolidine and Its Conformation Based on NMR Spectrometry

K. BERG-NIELSEN
Kjemisk Institutt, Universitetet i Oslo, Oslo 3, Norway

The ring inversion of a five-membered ring is usually much faster than the pyramidal nitrogen inversion. In 1,2,4,4-tetramethylpyrazolidine the inversion about the two nitrogen atoms has been studied by NMR spectroscopy. At low temperature the protons at 3 and 5 position appeared as two identical AB quartets. The conoicentric temperature was found to be $-45^\circ\text{C}$ in dichloromethane and the inversion barrier $\Delta G^\ddagger = 11.1 \text{ kcal/mol}$. Inversion of pyramidal nitrogen passes through a planar transition state. The conjugation of the lone pair with a phenyl substituent is expected to give the nitrogen sites a more planar shape and to decrease the inversion barrier. This decrease may be calculated by the empirical equation:

$$\Delta G^\ddagger = \Delta G^\ddagger_z, Z_1$$

where $Z_1$ represents the substituent and $X$ the rest of the molecule. Choosing methyl as unity ($Z_{CH_3} = 1$) gives $\Delta G^\ddagger_{CH_3} = Z_{CH_3}$, where $Z_{CH_3}$ is found to be 0.59. The barrier to nitrogen inversion in 4,4-dimethyl-1,2-diphenylpyrazolidine may thus be calculated as $11.1 \times 0.59 \approx 6.55 \text{ kcal/mol}$.

Pyrazolidine-3-ones can be reduced by lithium aluminium hydride in a suitable solvent to the corresponding pyrazolines.

In continuation of our work with lithium aluminium hydride reduction of acyl hydrazobenzenes also 4-butyl-1,2-diphenylpyrazolidine-3,5-dione has now been reduced to 4-butyl-1,2-diphenylpyrazolidine (I).

The NMR shifts for $H_1$ and $H_2$ are temperature dependent. The difference between them, $\Delta \nu$, in Freon 21 is 0.93 ppm at $-90^\circ\text{C}$ and 0.84 ppm at $0^\circ\text{C}$. In carbon tetrachloride $\Delta \nu$ is 0.80 ppm at $0^\circ\text{C}$, 0.77 ppm at $29^\circ\text{C}$, and 0.72 ppm at $73^\circ\text{C}$, the coupling picture being the same.

Thus the nitrogen inversion is, as expected, too fast to give a low-temperature spectrum at $-90^\circ\text{C}$, which should correspond to a barrier lower than ca. 8.5 kcal/mol.

Since corresponding protons at $C_2$ and $C_3$ are identical at all temperatures, the rapid inversion must produce a plane of symmetry in the molecule perpendicular to and through the middle of the $N-N$ bond.

The difference in chemical shifts for $H_1$ and $H_2$, 0.77 ppm, is too large to be caused by the butyl group only; it must be due to shielding and deshielding effects of the benzene rings. The NMR spectra therefore indicate that the energy minimum of the ring corresponds to $C_1$ symmetry with the butyl group in "equatorial" position at the tip of the envelope.

Because of the butyl group all other conformations have higher energy. Their population must increase somewhat with temperature to explain the decrease in $\Delta \nu$ between $H_1$ and $H_2$. Possibly some kind of solvent interaction is also involved.

1,2-Diphenylpyrazolidine has no substituents at $C_2$ providing energy difference of this kind. In its NMR spectrum the $H_1$ and $H_4$ protons therefore appear as a triplet at $3.43$, $J = 6.5 \text{ Hz}$ showing that they are equal. The protons at $C_2$ appear as a quintet at $1.94$.

Models of 4-butyl-1,2-diphenylpyrazolidine (II and III) suggest a difference in shielding and deshielding effects at $H_1$ and $H_2$ in good agreement with the found values (Fig. 1). When the adjacent phenyl group is trans to $H_4$(II), this proton will be very near to the plane of the benzene ring and therefore in the deshielding zone. At the same time $H_1$ will be in the shielding zone. The other phenyl group is more remote and gives a smaller effect, only a slight shielding effect at $H_1$. When the adjacent phenyl group is trans to $H_1$, (III), the distance from the ring to $H_1$ is greater and the deshielding effect will be reduced. $H_1$ in (III) will be less shielded than $H_1$ in (II). The other phenyl group gives only a slight shielding effect at $H_1$.

An inspection of a model of this molecule.
Table 1. The NMR spectrum of (I) in carbon tetrachloride at 29°C in δ values.

<table>
<thead>
<tr>
<th>C₆H₆</th>
<th>H₁</th>
<th>H₂</th>
<th>H₃</th>
<th>H₄</th>
<th>C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.25–6.64</td>
<td>10 H</td>
<td>2.93t</td>
<td>2H</td>
<td>3.70d</td>
<td>2H</td>
</tr>
</tbody>
</table>

t = triplet, d = 2 doublets, c = complex; J₁₂ = 9.8 Hz, J₁₃ = 9.4 Hz, J₃₄ = 7.0 Hz.

![Diagram of molecules (II) and (III)]

Fig. 1. Models of 4-butyl-1,2-diphenylpyrazolidine showing shielding and deshielding effects of the benzene rings at H₁ and H₂.

also shows that the dihedral angle between H₁ and H₂, θ₁₂, is closer to 180° than the dihedral angle between H₃ and H₄, θ₃₄, is close to zero. The observed coupling constants J₁₂ = 9.4 Hz > J₃₄ = 7.0 Hz are therefore in agreement with values predicted from the Karplus equation.

Experimental. Melting points were determined on a micro hot-stage. NMR spectra were recorded on a Varian A-60 A and HA 100. Spectrometers with tetramethylsilane as internal reference, mass spectra on a AEI/EC MS 902 instrument, and infrared spectra on a Perkin-Elmer 457 Grating Infrared Spectrophotometer. Thin layer chromatography was used with toluene as eluent and iodine vapour as staining reagent.

4-Butyl-1,2-diphenylpyrazolidine (I). To a solution of 4-butyl-1,2-diphenylpyrazolidine-3,5-dione (6.2 g, 20 mmol) in dry ether (40 ml) was added a suspension of lithium aluminium hydride (2.7 g, 70 mmol) in dry ether (40 ml), and the mixture was refluxed for 2 h. After cooling, water (5 ml) was added cautiously and then 2 N sodium hydroxide (2 ml). After 30 min the solid material was filtered off and the solution dried with calcium chloride. The ether was removed at low pressure and the product purified by column chromatography on aluminiun oxide with toluene as eluent. The yield was 1.8 g (31%) of a liquid which was not further purified. It was kept at ~10°C to avoid darkening. The IR spectra showed no absorption due to carbonyl. The mass spectrum showed m/e = 280.

1,2-Diphenylpyrazolidine. A dispersion of hydrazobenzen (6.3 g, 33 mmol), 1,3-diodopropane (9.7 g, 33 mmol), and sodium hydrogen carbonate (5.7 g, 66 mmol) in ethanol (200 ml) was refluxed with stirring under nitrogen for 22 h. Undissolved sodium iodide (2.4 g) was filtered off and the solvent removed at low pressure, leaving a solid residue (13 g). This was extracted with toluene (3 x 15 ml) giving more undissolved sodium iodide (3.2 g). The toluene was evaporated in vacuo, and the solid residue was extracted thoroughly with petrol ether, b.p. 60–80°C (4 x 15 ml), leaving hydrazobenzen undissolved (4.8 g). The petrol ether was removed at low pressure, and the residue solidified on cooling. It was then washed with some petrol ether (3 x 4 ml) leaving 0.9 g (13%) of a white product, m.p. 99.5–100.5°C after crystallization from ethanol. (Lit. 96–98°C* and 98.5–99°C'.) The mass spectrum showed m/e = 224.


Received February 6, 1973.