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

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The ring inversion of a five-membered ring is usually much faster than the pyramidal nitrogen inversion.[1] In 1,2,4,4-tetramethylpyrazolidine the inversion about the two nitrogen atoms has been studied by NMR spectroscopy.[1] At low temperature the protons at 3 and 5 position appeared as two identical AB quartets. The coalescence temperature was found to be $-45°C$ in dichloromethane and the inversion barrier $\Delta G^{\neq} = 11.1$ kcal/mol.

Inversion of pyramidal nitrogen passes through a planar transition state.[2] 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 [3]

$$\Delta G^{\neq}_1 = XZ = \Delta G^{\neq}_{CH_3} Z_1$$

where Z_1 represents the substituent and X the rest of the molecule. Choosing methyl as unity $(Z_{CH_3} = 1)$ gives $\Delta G^{\neq}_{C_6H_5} = \Delta G^{\neq}_{CH_3} Z_{C_6H_5}$ where $Z_{C_6H_5}$ is found to be 0.59.[6] The barrier to nitrogen inversion in 4,4-dimethyl-1,2-diphenylpyrazolidine may thus be calculated as $11.1 \times 0.59 \sim 6.55$ kcal/mol.

Pyrazolidine-3-ones can be reduced by lithium aluminium hydride in a suitable solvent to the corresponding pyrazolidines.[4-6]

In continuation of our work with lithium aluminium hydride reduction of acyl hydrazobenzenes [7] also 4-butyl-1,2-diphenylpyrazolidine-3,5-dione has now been

(I)

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 $-90°C$ and 0.84 ppm at $0°C$. In carbon tetrachloride $\Delta\nu$ is 0.80 ppm at $0°C$, 0.77 ppm at $29°C$, and 0.72 ppm at $73°C$, the coupling picture being the same.

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

Since corresponding protons at C_3 and C_5 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_s 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_4 providing energy difference of this kind. In its NMR spectrum the H_1 and H_2 protons therefore appear as a triplet at δ 3.43, $J = 6.5$ Hz showing that they are equal. The protons at C_4 appear as a quintet at δ 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_2(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_2. 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_2 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
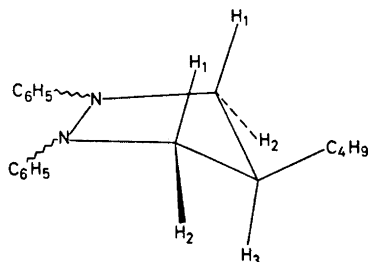
Table 1. The NMR spectrum of (I) in carbon tetrachloride at 29°C in δ values.

C_6H_5		H_1		H_2		H_3		C_4H_9	
8.25 − 6.64	10 H	2.93t	2H	3.70d	2H	~2.3c	1H	0.86t	3H
								1.31c	6H

t = triplet, d = 2 doublets, c = complex; $J_{1,2} = 9.8$ Hz, $J_{1,3} \approx 9.4$ Hz, $J_{2,3} = 7.0$ Hz.

(II)   (III)

H_1 shielded H_1 slightly deshielded

H_2 deshielded H_2 slightly shielded
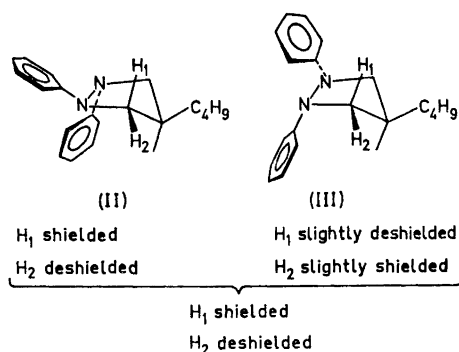
H_1 shielded

H_2 deshielded

Fig. 1. Models of 4-butyl-1,2-diphenylpyra-zolidine showing shielding and deshielding ef-fects of the benzene rings at H_1 and H_2.

also shows that the dihedral angle between H_1 and H_3, $\theta_{1,3}$, is closer to 180° than the dihedral angle between H_2 and H_3, $\theta_{2,3}$, is close to zero. The observed coupling constants $J_{1,3} = 9.4$ Hz $> J_{2,3} = 7.0$ Hz are therefore in agreement with values pre-dicted from the Karplus equation.

Experimental. Melting points were de-termined on a micro hot-stage. NMR spectra were recorded on Varian A-60 A and HA 100 Spectrometers with tetramethylsilane as in-ternal reference, mass spectra on an AEI/EC MS 902 instrument, and infrared spectra on a Perkin-Elmer 457 Grating Infrared Spectro-photometer. 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 alumi-

nium 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 absorp-tion due to carbonyl. The mass spectrum showed $m/e = 280$.

1,2-Diphenylpyrazolidine. A dispersion of hydrazobenzene (6.3 g, 33 mmol), 1,3-diiodo-propane (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 × 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 × 15 ml), leaving hy-drazobenzene 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 × 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 [9] and 98.5 − 99°C [10].) The mass spectrum showed $m/e = 224$.

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