Nuclear Quadrupole Double Resonance of Compounds with Transannular Boron–Nitrogen Bonds*

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The boron and nitrogen nuclear quadrupole double resonance spectra of several ring compounds with transannular boron–nitrogen bonds are reported. The electron donation from nitrogen to boron as seen by their quadrupole coupling parallels the boron–nitrogen bond lengths. One of the compounds exhibits a transannular valence topomerisation between two identical boron–nitrogen pairs in solution which is frozen in the solid state but may possibly exist in a preformed state of this equilibrium from its quadrupole coupling. The oxygen-boron π-bond in boroxines, whose extent is deduced from the quadrupole coupling in one of the compounds with a boroxine-like structure at boron and in $(PhBO)_3$, is approximately half as strong as the nitrogen–boron π-bond in borazine.

Introduction

The recently synthesised and characterised compound I (Fig. 1) [1] shows the remarkable property of valence-topomerisation of its boron–nitrogen bonds: as evidenced by NMR, there is a dynamical equilibrium between the two equivalent forms of I in solution, with the boron–nitrogen bonds being alternately broken and reestablished. In the solid state, only one form exists with an extraordinarily long (1.74 Å) boron–nitrogen bond [2]. The boron–nitrogen bond lengths in comparable compounds with transannular boron–nitrogen bonds and similar bonding partners are 1.67 Å (in II (Fig. 2) [3]) and 1.65 Å (in III (Fig. 2) [4]).

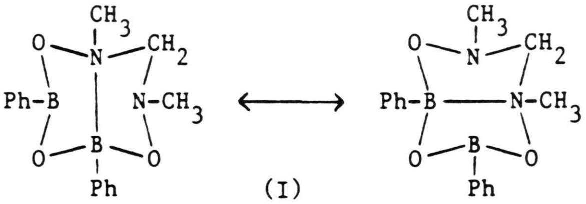

Fig. 1.

We have observed the nuclear quadrupole double resonance spectra of I, II, and III in order to obtain information on the electronic structure of such transannular boron–nitrogen bonds, and especially to compare the weak B–N bond in I with those in II and III. Furthermore, I contains two pairs of boron and nitrogen atoms, the one pair only differing by its additional B–N bond from the other. Thus, a comparison of the n.q.r. data of the two pairs seemed to be especially appropriate for the elucidation of the properties of the boron–nitrogen bond. Since the bonding configuration at boron in IV (Fig. 2) is similar to that in I, it was included in this series.

Experimental

The nuclear quadrupole double resonance spectra were observed at room temperature by both "level crossing" and "cross relaxation" techniques [5]. The latter method detected only the nitrogen transitions so that the boron and nitrogen lines in the "level crossing" spectra could be assigned easily. The results of our measurements are collected in Table 1.

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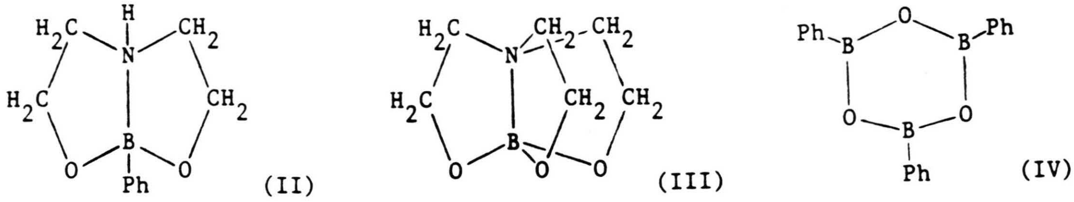

(II) (III) (IV)

Fig. 2.

Interpretation

The assignment of the experimentally found coupling constants to the two different boron atoms in I is not difficult, because the coupling constant of the tricoordinate boron is known approximately from the similar boron of IV and that of the tetracoordinate boron from II. No comparison of this kind is possible for nitrogen, because the substituents at this nucleus are too different in I and the other compounds of the series. The coupling constants in several hydroxyl-ammonium chlorides [6]

$$[MeH_2NOH]Cl, [H_3NOH]Cl, [H_3NOEt]Cl$$

lie between 3.9 and 4.1 MHz, the coupling constants of N-hydroxy-piperidine and H_2NOMe at 5.9 MHz [7]. This suggests the assignment of the coupling constant of 3.899 MHz to the tetracoordinate nitrogen in I on account of its similarity to the nitrogen in the hydroxyl-ammonium chlorides. The coupling constant of the tricoordinate nitrogen in I is then significantly smaller than in the two reference compounds in the literature.

The higher coupling constant of the tricoordinate boron in IV compared to that in I appears to be due to less filling of the π-hole at boron in IV, because there is only one oxygen per boron in IV whereas two oxygens can donate π-density to boron in I. It is interesting to compare the extent of π-bonding in boroxine with that in borazine [8]. According to previous PPP calculations [9], the π-bonding of the phenyl group to boron is negligible so that the π-bonding from oxygen to boron in boroxine as estimated by means of a Townes-Dailey analysis is approximately half as strong as it is from nitrogen to boron in borazine.

The decrease in the coupling constants of the tetracoordinate borons in the series I, II, III parallels the decrease in the boron–nitrogen bond lengths. This trend seems to be due to an increasing donation of electron density from nitrogen to boron.

Table 1. Summary of the n.q.r. measurements (all frequencies in kHz).

N

Compound		ν_+	ν_-	ν_0	e^2qQ/h	η
I	tri	4390 (10)	2460 (10)	1920 (10)	4567 (10)	0.845 (6)
	tetra	3606 (10)	2242 (10)	–	3899 (10)	0.700 (7)
II		2000 (10)	1290 (10)	700 (10)	2190 (10)	0.64 (1)
III		2160 (5)	–	–	2880 (5)	0

B

Compound		^{10}B (7 ↔ 1,6 ↔ 1)	^{10}B (7 ↔ 3,6 ↔ 3)	^{11}B	further lines		e^2qQ/h (^{11}B),	η
I	tri	2958 (20)	2057 (20)	1542 (10)	3086 (10) ^{11}B^{11}B	2517 (10) ^{11}B^{11}B	2879 (20)	0.70 (5)
	tetra	1818 (20)	1276 (20)	970 (10)	1931 (10) ^{11}B^{11}B		1798 (20)	0.70 (5)
II		1470 (20)	1140 (10)	780 (20)	1690 (20) ^{11}B^{11}B		1547 (20)	0.50 (5)
III		1180 (20)		620 (5)			1240 (10)	
IV		3125 (15)	2310 (10)	1654 (5)	1448 (10) ^{10}B		3148 (20)	0.56 (2)

The coupling constant of the tricoordinate nitrogen in I (4.6 MHz) is clearly smaller than in the reference compounds N-hydroxypiperidine and H_2NOCH_3 (5.9 MHz). This phenomenon could be due to a decrease of electron density in the "lone pair" orbital of nitrogen. Close intermolecular contacts between the nitrogen atom and other atoms in the crystal do not exist [2], so that only intramolecular transfers of electron density can be considered. It is interesting to speculate on the possibility of weak bonding between the cusps of the bow-shaped molecule, linking the tricoordinate nitrogen and the tricoordinate boron, in addition to the bond of the other boron−nitrogen pair. In solution, the two contribute equally to the B−N bonding.

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