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ELECTRONIC EFFECTS IN BORAZINES: AN NMR STUDY

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Summary

The proton NMR spectra of hexamethylborazine, *B*-monoethylpentamethylborazine, *B,B'*-decamethylbiborazine, *B*-pentamethylphenylpentamethylborazine and decamethylbiphenyl were studied in an attempt to elucidate the electronic effects in the borazine ring systems. A discussion of the possible sources of the anisotropy of the borazine ring is presented.

Introduction

The internal electron-donation in and diamagnetic anisotropy of the borazine ring has been of considerable interest. The possibility of resonance stabilization in borazines and the existence of benzenoid type canonical structures [1] suggests that borazine—benzene analogies exist. We present here an attempt to measure directly the shielding anisotropy of a borazine ring relative to a similarly substituted benzene ring at comparable points in space above and below the respective ring systems, using a set of isostructural, near-rigid molecules. Internal coordination or donation of electrons from the nitrogen atom to the boron atom in borazines and in methylamine—boranes was estimated by a correlation method using NMR techniques.

Experimental

All spectra were recorded at ambient temperature on a Varian A-60 spectrometer at 60 MHz frequency. The chemical shifts are reported in Hz downfield from an internal standard of tetramethylsilane in benzene and in carbon tetrachloride as solvents. Preliminary studies showed that concentration-dependent chemical shifts of about 2 Hz occur at concentrations greater than 15%. Consequently all spectra reported here were recorded in the concentration range 8—5%; these spectra are comparable to the results obtained at infinite dilution. Instrumental error was less than 1.0 Hz over a 500 Hz sweep. The chemical shifts (± 0.2 Hz) are average values obtained from several spectra recorded for each compound.

The preparation of hexamethylborazine, *B*-monoethylpentamethylborazine, *B,B'*-decamethylbiborazine and *B*-pentamethylphenylpentamethylborazine are described elsewhere [2]. Hexamethylbenzene (Eastman Organic Chemicals) was used as received without further purification.

Decamethylbiphenyl

This was prepared by exhaustively methylating biphenyl using a modification of the method of Saunders et al. [3]. Pure decamethylbiphenyl was obtained after repeated recrystallization from absolute ethanol, m.p. 250—251.5°, in 1.7% yield. Found: C, 89.51; H, 10.56. $C_{22}H_{30}$ calcd.: C, 89.11; H, 10.68%.

Discussion

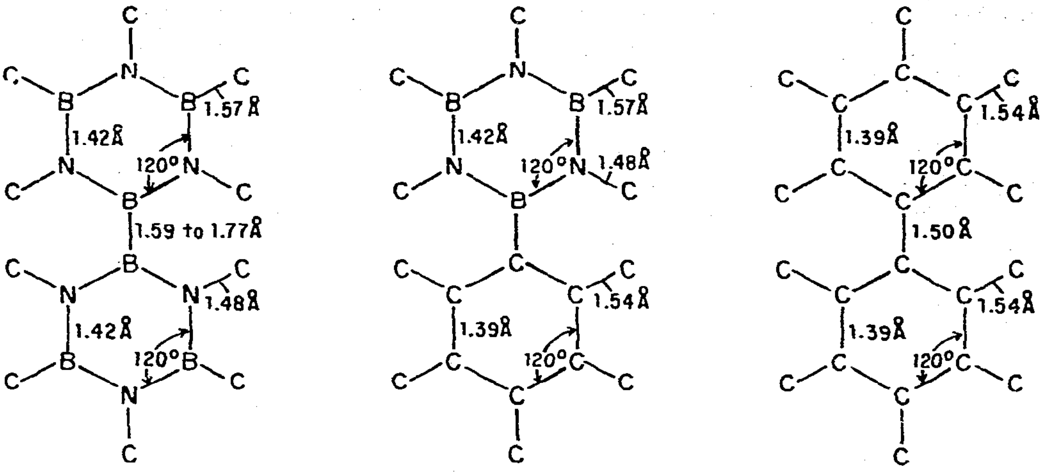
Shielding anisotropy of borazine

The shielding anisotropy effect of a phenyl group on an *N*-methyl group in 1,3,5-trimethyl-2,4,6-triphenylborazine has been used previously to determine the orientation of the phenyl groups with respect to the borazine ring [4]. The results indicate that these ring systems are perpendicular to each other. In this investigation the reverse strategy was used to measure the anisotropic shielding of a hexasubstituted borazine ring and a hexasubstituted benzene ring.

Substitution of biphenyl by methyl groups at the 2,6 and 2',6' positions leads to orthogonal ring systems with a large barrier to rotation [5]. Consideration of a molecular model of this compound suggests that the *ortho*-methyl groups on one ring extend into the anisotropic shielding zone of the other phenyl group which is consistent with the observed upfield shift of the methyl protons relative to that in toluene [4, 6]. Because benzene and borazine have very nearly the same geometrical parameters, it should be possible to investigate the anisotropic shielding of the borazine nucleus on *ortho*-methyl groups in a similar environment. Accordingly, *B,B'*-decamethylbiborazinyl, *B*-mono(pentamethylphenyl)pentamethylborazine and decamethylbiphenyl were prepared and their proton-NMR spectra determined. Although structural parameters are not known for these compounds, the assumption that they are isostructural with orthogonal ring systems is reasonable on the basis of the available data (Fig. 1).

The largest difference between C—C and B—N bond lengths for equivalent positions occurs in the B—B linkage in *B,B'*-decamethylbiborazinyl and the corresponding C—C distance in biphenyl which is between 0.07 and 0.25 Å depending on the B—B distance chosen as reference. The longer bond lengths (16.7%) for the B—B species should result in a weakening of the anisotropic shielding experienced by the *ortho*-methyl groups in that molecule.

The orientation of the rings, and the relative positions of the *ortho*-methyl groups in *B,B'*-decamethylbiborazinyl (I), *B*-pentamethylphenylpentamethylborazine (II) and decamethylbiphenyl (III) should be the same as in the 2,2',6,6'-tetramethylbiphenyl. Each of these compounds has the required *ortho,ortho'*-tetramethyl substitution pattern necessary to keep the respective rings orthogonal. In each member of this series of compounds there are two separate combinations of methyl groups that are shielded by a phenyl and by a borazine ring. Although the *para* or 4,4'-methyl substituents in compounds I, II and III may be used as "unshielded" references for the methyl proton chemical shift, hexamethylborazine



(I) (II) (III)

Fig. 1. Molecular parameters postulated for *B,B'*-decamethylbiborazinyl (I), *B*-mono(pentamethylphenyl)-pentamethylborazine (II), and decamethylbiphenyl (III) from available data from $(CH_3)_3N_3B_3H_3$ [8], $(C_2H_5)_6B_3N_3$ [9], B_2 [8], B_2Cl_2 [8], $(CH_3)_6C_6$ [8], $(C_6H_5)_2$ [10], $C_6H_5BCl_2$ [8], and $(CH_3)_3B_3O_3$ [8].

and hexamethylbenzene are also reasonable choices for standards, since both of these molecules contain methyl groups which are not shielded by another ring; the only shielding arises from the ring to which they are attached. Table 1 gives the methyl chemical shifts of compounds I, II and III as well as the standards in carbon tetrachloride and in benzene solutions. The *ortho*-methyl substituents in compounds I, II and III are upfield from the *para*-methyl substituents in

TABLE 1

CHEMICAL SHIFTS OF PERMETHYLATED ARENES AND BORAZINES

<table>
<tr><th rowspan="3">Compound</th><th rowspan="3">Solvent [a]</th><th colspan="6">Methyl [b] proton chemical shifts (Hz)</th></tr>
<tr><th colspan="3">Arene</th><th colspan="3">Borazine</th></tr>
<tr><th><i>ortho</i></th><th><i>meta</i></th><th><i>para</i></th><th><i>ortho(N)</i></th><th><i>meta (B)</i></th><th><i>para (N)</i></th></tr>
<tr><td>I</td><td>CCl_4</td><td></td><td></td><td></td><td>172.0</td><td>28.0</td><td>175.0</td></tr>
<tr><td></td><td>C_6H_6</td><td></td><td></td><td></td><td>177.0</td><td>31.5</td><td>171.0</td></tr>
<tr><td></td><td>Δ</td><td></td><td></td><td></td><td>−5.0</td><td>−3.5</td><td>+4.0</td></tr>
<tr><td>II</td><td>CCl_4</td><td>122.2</td><td colspan="2">129.0</td><td>154.8</td><td>30.0</td><td>177.8</td></tr>
<tr><td></td><td>C_6H_6</td><td>132.4</td><td colspan="2">129.0</td><td>164.5</td><td>31.8</td><td>171.3</td></tr>
<tr><td></td><td>Δ</td><td>−10.2</td><td colspan="2">0.0</td><td>−9.7</td><td>−1.8</td><td>+6.5</td></tr>
<tr><td>III</td><td>CCl_4</td><td>104.9</td><td colspan="2">132.8</td><td></td><td></td><td></td></tr>
<tr><td></td><td>C_6H_6</td><td>118.7</td><td>131.2</td><td>130.0</td><td></td><td></td><td></td></tr>
<tr><td></td><td>Δ</td><td>−13.8</td><td>+1.6</td><td>+2.8</td><td></td><td></td><td></td></tr>
<tr><td>$C_6(CH_3)_6$</td><td>CCl_4</td><td>128.8</td><td colspan="2">128.8</td><td></td><td></td><td></td></tr>
<tr><td></td><td>C_6H_6</td><td>127.0</td><td colspan="2">127.0</td><td></td><td></td><td></td></tr>
<tr><td></td><td>Δ</td><td>+1.8</td><td colspan="2">+1.8</td><td></td><td></td><td></td></tr>
<tr><td>B_3N_3-
$(CH_3)_6$</td><td>CCl_4</td><td></td><td></td><td></td><td>172.0</td><td>27.0</td><td>172.0</td></tr>
<tr><td></td><td>C_6H_6</td><td></td><td></td><td></td><td>167.5</td><td>29.2</td><td>167.5</td></tr>
<tr><td></td><td>Δ</td><td></td><td></td><td></td><td>+4.5</td><td>−2.2</td><td>+4.5</td></tr>
</table>

[a] Δ = chemical shift in CCl_4 solution minus the chemical shift in C_6H_6 solution. [b] Position of methyl groups given with reference to the atoms at which the rings are joined.

carbon tetrachloride solution. Substitution of a phenyl ring for a borazine ring produces essentially the same net upfield shift (i.e., 17.3 and 17.2 Hz) on the *ortho*-methyl group whether it is bound to the borazine ring (*N*-methyl) or to a phenyl ring.

The ratio fo the relative upfield shifts produced at an *ortho*-(*N*)-methyl group by substitution of a borazine ring and then a benzene ring for a *B*-methyl substituent on hexamethylborazine should give a term equal to the ratio, *R*, of the anisotropic shielding effects of the two ring system; *R* is defined by eqn. 1

$$R = \frac{\delta(\mathrm{Ref}) - \delta(\mathrm{I})}{\delta(\mathrm{Ref}) - \delta(\mathrm{II})} \qquad (1)$$

where δ is the chemical shift of the *ortho*-methyl protons in the species indicated in the brackets and the reference compounds are either hexamethylborazine or hexamethylbenzene. Likewise, the ratio of the relative upfield shifts produced at a *ortho*-methyl group by substitution by a borazine ring and then by a benzene ring for a methyl substituent on hexamethylbenzene should give a similar term provided that in all cases the molecules have similar structural parameters, inductive effects, and the coupled ring compounds have orthogonal ring systems. The results of these arguments show that these ratios are not equal, suggesting that our first assumptions must be modified. The first most obvious modification is one predicted earlier (Fig. 1), i.e. the length estimated for the B—B bond in compound I is indeed longer than the bond lengths for the corresponding B—C and C—C bond lengths estimated for compounds II and III respectively. The parameters given in Fig. 1 suggest that the second (arene) series should produce the more reliable data; however, this is much too simplistic a rationalization and corroborating evidence or compensating factors should be investigated.

In a prior publication [7] a correlation between both structural and electronic parameters with the "aromatic solvent induced shifts" (ASIS) for a series of substituted borazines was established. From the solvent shift data presented here (Table 1) it is apparent that minimal ASIS differences occur for the *meta* and *para* positions of either ring system in compounds I, II and III when compared to the ASIS differences of hexamethylborazine and hexamethylbenzene. These observations imply that the inductive effects of the three substituents CH_3, $(CH_3)_2B_3N_3(CH_3)_3$ and $C_6(CH_3)_5$, do not vary greatly in magnitude but generally follow the order of electron donation, viz., $(CH_3)_2B_3N_3(CH_3)_3 \geqslant CH_3 \geqslant C_6(CH_3)_5$. On the other hand, if the ASIS differences for those methyl protons in the *ortho* positions are examined, a large variation occurs which appears to follow a regular pattern. The ASIS difference for an *N*-methyl group on hexamethylborazine (+4.5 Hz) compared to the corresponding difference in hexamethylbenzene (+1.8 Hz) indicates that, according to the ASIS criteria, the *N*-methyl protons are more closely associated with the face of a benzene solvent molecule than the arene methyl groups and are shifted upfield to a greater extent. This difference might explain to some extent the decreased downfield ASIS of the *N*-methyl protons of compound II (—9.7 Hz) compared to the arene methyl protons of II (—10.2 Hz), but it cannot be reasonably used to explain the regular decrease in ASIS in the *ortho*-methyl protons of compounds I (—5.0 Hz), II (—9.7 Hz) and III (—13.8 Hz). [In this discussion a + sign indicates that the shift in question is upfield from the reference compound.] Steric repulsions, as it will be recalled, could account for a low ASIS but cannot explain the strong deshielding effect observed. Electron density arguments require that the *ortho*-methyl protons in compounds I, II and III be progressively more negative to account for the observed ASIS effect. The similar ASIS values for the *ortho-N-* (—9.7 Hz) and arene-methyl protons in compound II (—10.2 Hz) suggest that the main reason for the observed ASIS does not stem from local bonding differences, but instead from a property related to the individual ring systems and that the orthogonality of the rings does not eliminate the type of interaction necessary to give similar ASIS values in compound II.

If the observed effects stem from the π electron distribution in the rings, it becomes apparent that the borazine ring provides less electron density than a similarly substituted arene ring, at least at the boron site. If a difference in electron density affecting the ASIS of the *ortho*-methyl protons of compounds I, II and III also affects the chemical shift of those methyl protons relative to tetramethylsilane in carbon tetrachloride solution (thus competing with any anisotropic induced shifts observed in the substitution for methyl groups of substituted borazine and phenyl substituents) a very probable cause for the discrepancy observed in the calculated anisotropy ratios will have been found. The hypothesis that an electron density increase proportional to the magnitude of the ASIS differences in compounds I, II and III is a significant factor contributing to the chemical shifts of the respective *ortho*-methyl protons can be tested using anisotropy ratios as defined in eqn. 1. Hexamethylborazine and hexamethylbenzene were used as reference compounds; a correction factor calculated from the maximum ASIS found in compound III (—13.8 Hz) minus the respective ASIS of compounds I (—5.0 Hz) and II (—9.7, N-CH_3; —10.2 Hz, arene-CH_3) was added to the chemical shift values observed for the respective *ortho*-methyl protons (Table 1). The resulting anisotropy ratios are similar (0.41 for the compounds related to II and 0.43 for those related to III) suggesting that the increase in electron density is real and does, indeed, affect the chemical shift of the *ortho*-methyl protons. These results indicate that the anisotropy might not be caused by the so-called ring current, but might instead measure the shielding resulting from the p_z electron density of the atoms of the B—B, B—C, and C—C bonds linking the rings in compounds I, II and III. Formally the population of the p_z orbitals of the boron atoms is zero although electron density is presumably enhanced by donation from the adjacent nitrogen atoms. The decrease in ASIS is consistent with the formal p_z orbital population of the B—B, B—C and C—C bonds of 0, 1, and 2 p_z electrons. The non-zero ASIS of compound I is most likely associated with electron density resulting from donation of electrons to the boron by adjacent nitrogen atoms in the borazine ring.

Acknowledgement

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