Crystal structure, $^1$H and $^{13}$C NMR spectral studies of 1,2,4,5-oxadiazaborole derivatives

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1. Introduction

In medicinal chemistry, boron compounds have great potential in drug discovery. These compounds have been reported in the literature as having potential biological activities [1-5]. Some of these are: heterocyclic aminoboron compounds (antituberculosis agents) [6], boron-containing GSK2251052 (antimicrobial agent) [7], oxaboroles (antibacterial prototypes) [8], α-amino cyclic boronates (inhibitors of HCV NS3 protease) [9], benzoxaboroles (anti-inflammatory agents) [10], boronic acid esters (antibacterial agents) [11], boron-containing thiosemicarbazones (antifungal agents) [12], organoboron derivatives (antimicrobial and antifertility activities) [13] and aryl boronate esters (antimicrobial agents) [14]. The other heterocyclic systems containing B-N bonds also show biological activities. Hence, oxadiazaboroles should be interesting compounds for biological activity studies. When we consider the structure of 1,2,4,5-oxadiazaboroles, the presence of oxygen-, nitrogen- and boron- in the five-membered heterocycle system, it can be expected some physiological activities. In relation to this, the study of the transmission of substituent effects on these heterocycles may provide better insight for their structure-activity relationships.

The chemical shifts in $^1$H and $^{13}$C NMR spectra are often used for the study of the transmission of substituent effects on molecules. Analysis of the substituent chemical shifts (SCS) is based on Hammett or modified Hammett equations [15-18].

In this study, we calculated the $^1$H and $^{13}$C NMR chemical shifts of 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaboroles (1a-r) were studied respectively. Single and dual substituent parameters were used for the correlation analysis of substituent-induced chemical shifts with $\sigma$, $F$ and $R$ constants. The calculations have shown the polar and resonance substituent effects on N-H proton and C=N carbon atoms. The $p$ value was found positive for compounds (1a-r), which means that the substituent effect is normal. Additionally, crystal structure of compound (1i) was also studied. Density functional theory (DFT) calculations were carried out to calculate the theoretical chemical shifts, bond distances and bond angles.

ABSTRACT

Substituent effects on $^1$H and $^{13}$C NMR chemical shifts of 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaboroles (1a-r) were studied respectively. Single and dual substituent parameters were used for the correlation analysis of substituent-induced chemical shifts with $\sigma$, $F$ and $R$ constants. The calculations have shown the polar and resonance substituent effects on N-H proton and C=N carbon atoms. The $p$ value was found positive for compounds (1a-r), which means that the substituent effect is normal. Additionally, crystal structure of compound (1i) was also studied. Density functional theory (DFT) calculations were carried out to calculate the theoretical chemical shifts, bond distances and bond angles.

SCS = $p\sigma + q$ (1)

SCS = $p_1\sigma_f + p_2\sigma_r + q$ (2)

In the equations, $\sigma$ is Hammett substituent constant [18], $p$ shows the sensitivity of $^1$H and $^{13}$C NMR chemical shifts to substituent effects, $\rho_f$ and $\rho_r$ give the information about nonconjugative and conjugative effects respectively and $q$ is the intercept. $\rho_f$ and $\rho_r$ are relative measures of the transmission of inductive and resonance effects through the system. When a fit correlation with equation (1) is obtained, the use of equation (2) shows the nonconjugative ($\rho_f$) and conjugative effects ($\rho_r$).

Additionally, crystal structure of compound (1i) was also studied.

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Figure 1. Structure of 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaboroles (1a-r).

Table 1. Crystal data and structure refinement parameters for 5-(4-bromophenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (1i).

| Empirical formula | C_{13}H_{10}BBN_{2}O |
|-------------------|----------------------|
| Formula weight    | 300.95               |
| Crystal system    | Triclinic            |
| Space group       | P-1                  |
| \(a\) (\(\AA\))   | 5.597 (4)            |
| \(b\) (\(\AA\))   | 7.624 (4)            |
| \(c\) (\(\AA\))   | 15.296 (9)           |
| \(a^{\circ}\)      | 75.92 (2)            |
| \(\beta^{\circ}\)  | 84.21 (3)            |
| \(\gamma^{\circ}\) | 89.64 (3)            |
| \(V\) (\(\AA^3\))  | 629.8 (7)            |
| \(Z\)              | 2                    |
| \(D_v\) (\(g\ cm^{-3}\)) | 1.587               |
| \(\mu\) (\(\mu\ m\)) | 3.25                |
| \(\theta\) range (\(^\circ\)) | 3.4-28.6            |
| Measured refls.   | 11406                |
| Independent refls.| 2342                 |
| \(R_{int}\)        | 0.063                |
| \(S\)              | 1.18                 |
| R1/wR2             | 0.096/0.281          |

The molecular structure of 1i with the atom labeling is shown in Figure 2. The central ring make dihedral angles of 29.15(35)\(^\circ\) and 25.92(39)\(^\circ\) with the two phenyl rings. The dihedral angle of the phenyl rings is 54.25(28)\(^\circ\). Molecules of 1i are linked into sheets by the combination of N-H...N hydrogen bonds, C-H...π and π...π interactions (Tables 3 and 4). Atom N1 atom acts as hydrogen-bond donor, via atom H1, to atom N2 in the molecule at (x+1, y, z), forming a C(4) chain running which is parallel to the a axis (Figure 3). Compound (1i) also contains four C-H...π and one π...π interactions. An intermolecular π...π contact occurs between the two symmetry-related rings of neighbouring molecules. The distance between the ring centroids is 3.563(5) \(\AA\). The combination of C-H...π and π...π interactions produce 3D supramolecular network.

3.2. Substituent effects on \(^{13}\)C=N and \(^1\)H-N chemical shifts of (1a-r)

We have also obtained experimental and theoretical \(^{13}\)C and \(^1\)H NMR chemical shifts of C=N carbon and N-H proton in 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaboroles (1a-r). Computer aid is ranging from molecular design to architectural design [19,20] and also helps to control the experimental data. Therefore, we performed density functional theory (DFT) calculations on compounds (1a-r) to characterize their three-dimensional structures, predict their \(^{13}\)C=N and \(^1\)H-N chemical shifts.

3.1. X-Ray diffraction analysis

Compound (1i) was crystallized from acetone-hexane mixture, yielding single crystals for X-ray diffraction analysis. Suitable crystal of 1i was selected for data collection which was performed on a Bruker D8 QUEST diffractometer equipped with a graphite-monochromatic Mo-K\(_\alpha\) radiation at 296 K. The structure was solved by direct methods using SHELXS-97 [27] and refined by full-matrix least-squares methods on \(F^2\) using SHELXL-97 [27] from within the WINGX [28] suite of software. Hydrogen atoms bonded to C and N were refined using a riding model, with C-H=0.93 Å and N-H=0.86 Å. Molecular diagrams were created using MERCURY [29]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [30]. Details of data collection and crystal structure determinations and selected atomic parameters are given in Tables 1 and 2.

The distance between the two symmetry-related rings of neighbouring molecules. The distance between the ring centroids is 3.563(5) \(\AA\). The combination of C-H...π and π...π interactions produce 3D supramolecular network.
dihydro-1,2,4,5-oxadiazaboroles (1a-r) (Figure 1) to search the factors that affect the change of the chemical shifts. The correlations between the experimental and theoretical values gave fair results (Table 5); \( r^2 \): 0.812 (for \(^{13}\text{C}\) chemical shifts) and \( r^2 \): 0.670 (for \(^{1}\text{H}\) chemical shifts). The values of \(^{13}\text{C}\)N=N and \(^{1}\text{H}\)N refer to the center peak of DMSO-\(d_6\) which have the values of 39.50 ppm and 2.50 ppm for \(^{13}\text{C}\) and \(^{1}\text{H}\) respectively.

The aromatic \(^{1}\text{H}\) NMR and \(^{13}\text{C}\) NMR chemical shifts, measured for oxadiazaborole compounds (1a-r) [21] are given in Table 6.

Table 2. Selected bond distances (Å) and angles (º) for 5-(4-bromophenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (1i).

| Bond distances (Å) | Experimental (X-ray) | Calculated (DFT) |
|-------------------|----------------------|------------------|
| C8-B1             | 1.587(15)            | 1.521            |
| B1-N1             | 1.388(14)            | 1.443            |
| C7-N1             | 1.392(13)            | 1.359            |
| C9-C10            | 1.404(15)            | 1.394            |
| B1-O1             | 1.411(15)            | 1.411            |
| C7-N2             | 1.300(14)            | 1.355            |
| C11-Br1           | 1.906(10)            | 1.869            |
| N2-O1             | 1.480(11)            | 1.358            |

| Bond angles (º)   | Experimental (X-ray) | Calculated (DFT) |
|-------------------|----------------------|------------------|
| N2-C7-N1          | 116.8(10)            | 111.3            |
| N1-B1-O1          | 106.8(9)             | 103.7            |
| B1-N1-C7          | 105.3(9)             | 107.1            |
| N2-C7-C1          | 118.0(9)             | 120.4            |
| N1-B1-C8          | 132.2(10)            | 133.1            |
| C7-N2-O1          | 102.1(8)             | 106.9            |
| N1-C7-C1          | 125.2(9)             | 128.2            |
| O1-B1-C8          | 120.8(9)             | 123.0            |
| B1-O1-N2          | 108.9(8)             | 110.8            |

| Dihedral angles (º) | Experimental (X-ray) | Calculated (DFT) |
|---------------------|----------------------|------------------|
| C9-C8-B1-N1         | −23.0(2)             | 0.0              |
| C2-C1-C7-N1         | −29.4(15)            | 0.0              |

Table 3. Hydrogen-bond parameters for 1i (Å, º).

| D-H:···A            | D-H | H···A | D···A | D-H···A |
|---------------------|-----|-------|-------|---------|
| N1—H1···N2          | 0.86| 2.56  | 3.421 | 177     |
| C3—H3···Cg(3)\(^{ii}\) | 0.93| 2.86  | 3.523 | 130     |
| C6—H6···Cg(3)\(^{iii}\) | 0.93| 2.89  | 3.544 | 128     |
| C10—H10···Cg(2)\(^{iv}\) | 0.93| 2.86  | 3.540 | 131     |
| C13—H13···Cg(2)\(^{v}\) | 0.93| 2.87  | 3.555 | 131     |

Symmetry code: (i) x+1, y, z; (ii) 2-x, -y, 1-z; (iii) 1-x, 1-y, 1-z; (iv) 2-x, 1-y, 1-z; (v) 1-x, -y, 1-z; Cg(2)=C1-C6; Cg(3)=C18-C13

Table 4. \(\pi\)···\(\pi\) interaction distances for 1i (Å).

| Cg(I) | Cg(J) | Perpendicular distance |
|-------|-------|------------------------|
| Cg(1) | Cg(1) | 3.723(8)               |
| Cg(1) | Cg(1) | 3.563(5)               |

Symmetry code: (i) 1-x, -y, 1-z; Cg(1)=C1/N2/C7/N1/B1

Correlations of \(^{13}\text{C}\) and \(^{1}\text{H}\) NMR chemical shifts of C=N carbon and N-H proton with \(\sigma\) were done. The good fits with positive \(\rho\) values were obtained (Table 7). This shows that the changes in the electron density at C=N carbons and N-H protons are normal and not reverse [31-35]. This means that the substituent dipoles can not polarize \(\pi\)-units (as localized systems) through the space, because of the long distance.

In order to determine the relative importance of substituent resonance and field effects, DSP (dual sub-
stituent parameter) analyses of the $^{13}$C=N and $^1$H-N chemical shifts were carried out. The $\rho_F$ and $\rho_R$ values are given in Table 8 (F and R substituent constants are taken from [18]). As given in Table 8, $\rho_R$ values are greater than the corresponding $\rho_F$ values. This shows that C=N carbon and N-H proton in the heterocyclic ring are more sensitive towards the substituent resonance effects through resonance Structures III, IV and V (Figure 5) rather than polar substituent effects (Figure 4, Structures I and II).

Table 5. $^1$H-N and $^{13}$C=N NMR chemical shifts (in ppm) of 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaboroles (1a-r) (experimental/theoretical).

| Compounds | X          | $\gamma$ C=N (ppm) | $\gamma$ N-H (ppm) |
|-----------|------------|---------------------|---------------------|
| 1a        | p-N(CH$_3$)$_2$ | 156.974             | 9.231               |
|           | p-OH       | 159.115             | 9.265               |
|           |            | 155.339             | 8.108               |
| 1b        | p-OH       | 159.149             | 9.397               |
| 1c        | p-CH$_3$   | 159.206             | 9.467               |
|           |            | 156.028             | 8.197               |
| 1d        | m-N(CH$_3$)$_2$ | 159.231            | 9.447               |
|           | m-CH$_3$   | 159.259             | 9.489               |
| 1e        | H          | 159.267             | 9.533               |
| 1f        | m-N(CH$_3$)$_2$ | 159.276            | 9.457               |
| 1g        | m-OCH$_3$  | 159.038             | 9.533               |
| 1h        | m-N(CH$_3$)$_2$ | 159.236            | 9.447               |
| 1i        | m-CH$_3$   | 159.259             | 9.489               |
| 1j        | m-N(CH$_3$)$_2$ | 159.267            | 9.533               |
| 1k        | m-CH$_3$   | 159.259             | 9.489               |
| 1l        | m-N(CH$_3$)$_2$ | 159.267            | 9.533               |
| 1m        | p-Br       | 159.294             | 9.626               |
| 1n        | p-Br       | 159.294             | 9.626               |
| 1o        | m-Br       | 159.278             | 9.701               |
| 1p        | p-Br       | 159.278             | 9.701               |
| 1r        | m-Br       | 159.278             | 9.701               |
| r         |            | 0.812               | 0.670               |

a) Except m-N(CH$_3$)$_2$ (1e); b) Except m-N(CH$_3$)$_2$ (1e) and m-OCH$_3$ (1h); r. Correlation coefficient

Figure 3. Crystal structure of 1i, showing the formation of a chain along a axis generated by N-H···N hydrogen bonds.

Table 5. $^1$H-N and $^{13}$C=N NMR chemical shifts (in ppm) of 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaboroles (1a-r) (experimental/theoretical).
Table 6. Aromatic 1H and aromatic 13C NMR chemical shifts (in ppm) of 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiaza boroles (1a-r) (experimental).

| Compounds (Substituent, X) | 1H (ppm) | 13C (ppm) |
|---------------------------|----------|-----------|
| Ta (p-N(CH3)2)            | 7.095-7.063, 6.882, 6.678-6.651, 5.917 | 152.098, 135.169, 130.564, 128.896, 126.994, |
| Tb (p-OH)                 | 7.040-7.007, 6.853-6.825, 6.633-6.610, 5.975-5.946 | 160.177, 135.829, 130.713, 128.991, 126.895, |
| Tc (p-OCH3)               | 7.084-6.973, 6.680-6.649, 6.183 | 161.627, 135.660, 130.689, 128.937, 126.806, |
| Td (p-Ch3)                | 7.078-7.047, 6.937, 6.662-6.641, 6.414 | 140.842, 133.965, 130.747, 128.979, 128.944, |
| Te (m-N(CH3)2)            | 7.083-7.030, 6.678-6.656, 6.483-6.339, 6.347-6.313 | 150.145, 130.787, 128.997, 128.894, 126.801, |
| Tf (m-Ch3)                | 7.079-7.032, 6.834-6.789, 6.648-6.616, 6.477-6.417 | 137.221, 134.509, 131.788, 131.028, 130.784, |
| Tg (H)                    | 7.085-7.021, 6.662-6.565 | 133.893, 131.111, 130.762, 128.967, 128.249, |
| Th (m-OCH3)               | 7.082-7.050, 6.674-6.495 | 159.037, 130.573, 129.371, 128.760, 126.440, |
| Tl (p-Br)                 | 7.099-7.067, 7.006-6.979, 6.872-6.838, 6.708-6.681 | 135.809, 131.359, 130.815, 128.979, 126.543, |
| Tj (p-Cl)                 | 7.066-7.040, 6.690-6.675 | 136.169, 135.642, 130.793, 128.964, 128.406, |
| Tk (m-Cl)                 | 7.069-7.038, 6.973, 6.684-6.626 | 133.374, 132.176, 130.909, 130.825, 130.371, |
| Tl (m-Br)                 | 7.426-6.639 | 139.261, 133.801, 132.522, 130.846, 130.685, |
| Tm (p-COCH3)              | 7.179, 7.100-7.068, 6.698-6.676 | 138.520, 134.129, 130.885, 129.024, 128.091, |
| Tn (m-CN)                 | 7.433, 7.336, 7.137-7.050, 6.865-6.813, 6.710-6.688 | 138.093, 137.357, 134.409, 130.927, 129.465, |
| To (m-NO2)                | 7.863, 7.487-7.390, 7.080-7.048, 6.924-6.871, 6.695-6.674 | 147.691, 139.997, 130.922, 129.975, 129.021, |
| Tp (p-SO2CH3)             | 7.294, 7.185, 7.084-7.052, 6.687-6.665 | 142.888, 134.770, 134.671, 130.983, 129.082, |
| Tr (p-NO2)                | 7.461, 7.298, 7.091-7.060, 6.692-6.677 | 128.119, 126.579, 126.455, 126.326, 125.665, |

Table 7. Statistical results of SSP (single substituent parameter) correlation analysis of 13C=N and 1H-NMR chemical shifts of (1a-r) against X.

| Bonds | r   | p   | q   | n   |
|-------|-----|-----|-----|-----|
| 13C=N | 0.880 | 0.289 | 159.22 | 17 |
| 1H-N  | 0.983 | 0.388 | 9.51  | 17 |

Table 8. Statistical results of DSP (dual substituent parameter) correlation analysis of 13C=N and 1H-NMR chemical shifts of (1a-r) against F and R constants.

| Bonds | r   | p_F | p_R | q   | p_F/p_R | n   |
|-------|-----|-----|-----|-----|---------|-----|
| 13C=N | 0.997 | 0.273 | 0.354 | 159.27 | 0.771  | 10  |
| 1H-N  | 0.987 | 0.388 | 0.412 | 9.53  | 0.942  | 10  |

Figure 4. The polar substituent effect in compounds (1a-r).
4. Conclusions

In this study, we have carried out the combined experimental and theoretical spectroscopic analysis of 5-substituted phenyl-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaboroles (1a-r), using $^1$H, $^{13}$C NMR techniques and DFT. In general, good correlations between experimental and calculated values have been observed. X-ray studies helped in establishing the structure with optimized geometric parameters (bond lengths, bond angles and dihedral angles) which are determined by DFT theory and compared with the experimental data. The substituent chemical shift (SCS) values with applied linear free energy relationships (LFERs) analysis were correlated with Hammett type substituent constants and substituent effects from the aryl groups were observed to be efficiently transmitted to the heterocyclic framework of the compounds. The $\rho_F/\rho_R$ values indicated that the resonance effect is significant at the C=N carbon and N-H proton of compounds (1a-r).

Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1454233. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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