Since the discovery of NMR coupling constants across hydrogen bonds \( {\text{A}}{\text{B}} \) containing nuclei with spin \( \frac{1}{2} \), such as \( {\text{A}} = {\text{F}}, {\text{B}} = {\text{N}} \) \( \text{[1–3]} \), it has been established that these NMR parameters can not only be used to detect hydrogen bridges in biomolecules \( \text{[4]} \) but also to determine the geometries of strong hydrogen bonds in solution. \( \text{[5]} \) It has been shown experimentally and by ab initio calculations \( \text{[1]} \) that scalar two-bond coupling constants \( 2J_{\text{AB}} \) attain maximum values when the \( {\text{A}}{\text{B}} \) distances are at a minimum. Whereas the maximum values have been established for \( \text{FHF} \) and \( \text{NHF} \) hydrogen bonds, the corresponding maxima are still unknown in the case of \( \text{NHN} \) bridges. To date, only \( 2J_{\text{N}N} \) values less than 11 Hz have been detected in nucleic acid base pairs \( \text{[3]} \) protonated sponges \( \text{[6,7]} \) and six- \( \text{[8]} \) and seven-membered \( \text{[9]} \) \( \text{H} \)-chelates. In contrast, DFT calculations gave maximum coupling constants \( 2J_{\text{NN}} = 25 \text{ Hz} \) \( \text{[5d]} \), corresponding to the shortest possible \( \text{N} \cdot \cdot \cdot \text{N} \) distance of about 2.5 {\text{Å}} \( \text{[10]} \). More reliable high-level coupled-cluster EOM calculations of small model systems predicted even larger coupling constants \( \text{[11,12]} \).

Herein we describe a novel class of anionic \( \text{H} \)-chelates with \( 15\text{N} \cdot \cdot \cdot 15\text{N} \) coupling constants of more than 16 Hz. These anions were obtained by deprotonation of 2,3-dipyrryl-2-ylquinoxalines (DPOs, Scheme 1). DPOs have been synthesized and studied as colorimetric anion receptors for charge-dense species, such as fluorine. \( \text{[13]} \) However, their unusual geometry makes it likely that their monodeprotonated forms would have unusually short \( \text{NHN} \) hydrogen bonds and thus unusually large \( 15\text{N} \cdot \cdot \cdot 15\text{N} \) coupling constants. This expectation has been realized, and we present herein the results of various NMR spectroscopy experiments and ab initio DFT calculations that characterize the geometries of the intramolecular \( \text{NHN} \) hydrogen bonds of these anions.

The \( \text{NHN} \) anions of the DPOs 1–3 were generated by treatment of solutions of the DPO precursors in 5:1 \( \text{CD}_2\text{Cl}_2 \) / [\( \text{D}_2 \)]\( \text{DMSO} \) mixtures to which small amounts of solid \( \text{NaH} \) were added. Minute quantities of dihydrogen were produced, along with the corresponding monoanion as the major organic product (see Experimental Section). [\( \text{D}_2 \)]\( \text{DMSO} \) was added to solvate the \( \text{Na}^+ \) cation, whereas solid \( \text{CD}_2\text{Cl}_2 \) was used as the primary solvent because it provided the reduced viscosity needed to carry out various NMR spectroscopic analyses at lower temperatures (conditions under which proton exchange was found to be slow).

Figure 1a shows the signals of the pyrrolic protons, labeled \( \text{H}1 \) and \( \text{H}17 \), of \( 15\text{N}_2 \) recorded at 233 K in \( \text{CD}_2\text{Cl}_2 \) / [\( \text{D}_2 \)]\( \text{DMSO} \). Under these conditions, two signals are observed, namely at 11.81 and 11.93 ppm. Each signal is split into a doublet, with coupling constants \( 1J_{\text{NH}} = -97.6 \) and \(-97.7 \text{ Hz} \).
respectively. These values are in accord with those recorded for pyrroles and porphyrins. The corresponding 15N{1H} NMR spectrum (Figure 1b) has two lines for the two pyrrole nitrogen atoms of [15N2]-2. No scalar coupling between the two 15N nuclei is observed, a finding that is consistent with the absence of intramolecular NHN hydrogen bonds.

In contrast, a single pyrrolic proton signal at 20.65 ppm is observed at 193 K for the monoanion [15N2]-2/C0 (Figure 1c). This signal is split into a pair of doublets, with values of $J_{N17H17} = 55.2$ and $J_{N1H1} = 24.7$ Hz. Unfortunately, we could not establish clearly whether these values are intrinsic or arise from a fast nondegenerate proton tautomerism between two tautomers $a$ and $b$ according to Scheme 1. We favor the latter possibility, as the values change slightly with temperature. The assignment of the coupling constants is tentative, and based on the assumption that [15N2]-2/C0 is energetically favored as corroborated by the DFT calculations described below. The average of both couplings is $40$ Hz, and the same value is observed for the symmetrical anion $3^{-}$ in [D8]DMSO at 298 K and natural 15N abundance. Values of $|−40|$ Hz or less have been predicted for short symmetrical NHN bonds.

The corresponding 15N{1H} NMR spectrum is depicted in Figure 1d. Again, two signals are observed. We ascribe the upfield signal to N17 and the downfield signal to N1. Their signal intensities are not equal as they experience different nuclear Overhauser effects. However, both signals appear as doublets, each with a coupling constant of $J_{NN} = 16.5$ Hz; this is the largest value recorded to date.

To characterize further the hydrogen bonds of the monodeprotonated DPQ anions derived from 1-3, we studied the effect of D-for-H isotope exchange on their respective NMR chemical shifts. Selected results are reproduced in Figure 2:

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**Figure 1.** Partial 1H and 15N NMR spectra of [15N2]-2 and its anion [15N2]-2/C0 dissolved in a mixture of CD2Cl2/[D6]DMSO (5:1): a) 1H signals of H1 and H17 of -2 at 233 K; b) 15N{1H} spectrum of [15N2]-2 at 233 K; c) 1H signal of [15N2]-2/C0 at 193 K; and d) 15N{1H} spectrum of [15N2]-2/C0 at 193 K.

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**Figure 2.** a) Partial 1H and 1H NMR spectra of a 0.02 m solution of [15N2]-2 in a mixture of CD2Cl2/[D6]DMSO (10:1) recorded at 233 K with a deuterium fraction $x_D=0.3$ in the labile (pyrrolic NH) proton sites. b) Partial 1H and 1H NMR spectra of the anion [15N2]-2/C0 obtained in a mixture of CD2Cl2/[D6]DMSO (5:1) after addition of solid NaH at 233 K. c) 1H{1H} NMR spectra of [15N2]-2 recorded at 193 K and at $x_D=0.3$; otherwise, the conditions were the same as in (c). d) 15N{1H} NMR spectra of [15N2]-2 recorded at 193 K and at $x_D=0.3$; otherwise, the conditions were the same as in (c).
The results presented in Figure 2e and f provide support for the notion that the anions 1 and 3, although symmetrical, are otherwise analogous to 2. The H chemical shifts, δ = 20.66 and 20.59 ppm, shift by −1.13 and −0.88 ppm, respectively, (i.e., upfield) after deuteration. Given this consistent and expected behavior, we did not synthesize and study the 15N isotopologues of these anions. To corroborate the estimated hydrogen-bond distances, we calculated the equilibrium geometries of all the anions using DFT ab initio methods. The results are shown in Table 1. The distances are calculated using DFT at the B3PW91/6-31+G* level.

Table 1: Equilibrium hydrogen-bond geometries of 1\(^-\), 2\(^-\), and 3\(^-\) calculated using DFT at the B3PW91/6-31+G* level.

<table>
<thead>
<tr>
<th>Anion</th>
<th>(r_{\text{H···N}}) [Å]</th>
<th>(r_{\text{N···N}}) [Å]</th>
<th>(\text{N–H···N Angle}[^\circ])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^-)</td>
<td>2.543</td>
<td>1.100</td>
<td>1.489</td>
</tr>
<tr>
<td>2(^a)</td>
<td>2.524</td>
<td>1.117</td>
<td>1.452</td>
</tr>
<tr>
<td>2(^b)</td>
<td>2.562</td>
<td>1.082</td>
<td>1.533</td>
</tr>
<tr>
<td>3(^-)</td>
<td>2.554</td>
<td>1.087</td>
<td>1.518</td>
</tr>
</tbody>
</table>

in the expected range, although a comparison with experimental values would require corrections for anharmonic zero-point vibrations. The energy of the tautomer 2\(^a\) was calculated to be about 5.9 kJ mol\(^{-1}\) larger than of 2\(^b\), a difference that supports the above-mentioned assignments for the 15N chemical shifts and the associated coupling constants \(J_{NN}\).

Several interesting questions arise. One of these is why the values of \(J_{NN}\) of the DPO anions are much larger than those of the related proton sponges.[6,7] Possible explanations are the differences in the overall charge of the systems, the hybridization of the nitrogen atoms, and the specific nature of the intermolecular interactions. Although further study is required, we do not think charge effects are dominant, as the chemical shifts of the hydrogen-bonded protons in both types of compounds are similar.

A second question is why the experimental values of \(J_{NN}\) for strong NHN hydrogen bonds are generally smaller than those expected from ab initio calculations. We believe that this result could reflect the observation[10] that the heavy-atom distances of the strongest and shortest hydrogen bonds are larger than those of the calculated equilibrium structures. This disparity arises from the space required by the hydrogen-bond proton for quantum zero-point vibrations,[11] an effect that leads eventually to a reduction in the \(J_{NN}\) value.

In conclusion, we have shown that deprotonation of 2,3-dipyrrrol-2-ylquinoxalines leads to hydrogen-bonded anions exhibiting the largest 15N–15N coupling constants observed to date. However, further efforts will be needed to quantify the relation between various observable NMR parameters and the geometry of strong NHN hydrogen-bonded systems.

**Experimental Section**

The NMR measurements were performed on a Bruker AMX 500 spectrometer operating at 500.13 MHz for \(^1\)H. The \(^{15}\)N spectra were measured using the standard pulse sequences, and using liquid CH₃NO₂, as reference, a species that resonates at 341.17 ppm relative to solid \(^{15}\)NH₄Cl.[39]

The synthesis of the DPOs was performed according to procedures described previously.[12,21] Doubly 15N-labeled analogues were prepared in a similar manner, starting from \(^{15}\)N-labeled pyrrole, which was enriched to about 95% with \(^{15}\)N.

The deprotonated DPO anions were generated in the NMR tubes used for analysis by adding small amounts of solid NaH to 0.01–0.02m DPO solutions in CD₂Cl₂/[D₆]DMSO (5:1). The formation of the anions was monitored by \(^1\)H NMR spectroscopy. The dianion 2\(^-\) could be observed in the presence of an excess of NaH, which was converted back into 2 (monitored by NMR spectroscopy) by adding trifluoroacetic acid. Deuteration of the exchangeable proton sites was achieved by dissolving the compounds in dichloromethane/D₂methanol.

Ab initio calculations were performed using the Gaussian 98 set of programs[28] at the B3PW91/6-31+G* level of density functional theory (DFT).[24]

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[16] The increase in solvent viscosity at lower temperatures and increased proton exchange at higher temperatures cause line broadening, which makes the determination of coupling constants difficult. At 233 K, for a sample prepared using tetra-butylammonium fluoride, we obtained values of –54.5 and –26 Hz.