

## X-RAY AND VIBRATIONAL STUDIES OF 8-AMINOQUINOLINE. EVIDENCE FOR A THREE-CENTER HYDROGEN BOND

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The x-ray structure of 8-aminoquinoline indicates that one of the NH bonds of the NH<sub>2</sub> group forms a three-center hydrogen bond, the major component being the intramolecular hydrogen bond and the minor component the intermolecular hydrogen bond. The IR and Raman spectra of 8-aminoquinoline and of its *N*-deuterated counterpart reflect the non-equivalence of the two NH(D) bonds and the weakness of the hydrogen bridge. © 1997 John Wiley & Sons, Ltd.

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### INTRODUCTION

Hydrogen bonding is one of the driving forces which determine three-dimensional structure and self-assembly in chemical and biological systems and the hydrogen bond pattern in model biological compounds has recently been reviewed and discussed.<sup>1</sup> The interest in 8-aminoquinoline (8-AQ), which contains functional groups commonly involved in hydrogen bonding, is related to its genotoxic activities such as mutagenicity<sup>2</sup> and to its unusually low proton acceptor ability in solution, much lower than that of 3-aminoquinoline.<sup>3</sup> This behavior has been accounted for by the existence of an intramolecular NH...N hydrogen bond which lowers the basicity of the nitrogen atom of the quinoline ring. The existence of an intramolecular hydrogen bond in solution was suggested by the non-equivalence of the two NH or ND bonds observed in the IR spectrum of the partially *N*-deuterated isotopomer. In order to confirm this statement, the x-ray structure of 8-AQ was determined in the present work. The Fourier transform (FT)-IR and FT-Raman spectra of the solid compound are also reported and discussed. Both techniques allow one to detect the presence of intra- and intermolecular interactions and to discuss their strength.

### EXPERIMENTAL

**Crystal data.** C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>, *M* = 144.17. Monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 6.884(1), *b* = 9.983(1), *c* = 10.425(1) Å, β = 91.45(1)°, *V* = 716.2(1) Å<sup>3</sup> (by least-squares refinement on diffractometer angles of 25 centered reflections, λ = 1.5178 Å), *Z* = 4, *D* = 1.337 mg cm<sup>-3</sup>. Transparent crystals, 0.40 × 0.20 × 0.20 mm, μ(Cu Kα) = 0.648 mm<sup>-1</sup>.

**Data collection and processing.** The following conditions were used: Siemens P4-PC diffractometer, graphite monochromatized Cu Kα radiation, θ–2θ mode, 1432 reflections collected (θ range for data collection between 6.14 and 54.23°, index range  $-1 \leq h \leq 7$ ,  $-1 \leq k \leq 10$ ,  $-10 \leq p \leq 10$ , 872 unique reflections (*R*<sub>merge</sub> = 0.034), no absorption correction applied.

**Structure analysis and refinement.** The structure was solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup>, with all-non hydrogen atoms anisotropic and hydrogens with isotropic temperature factors. Final *R* indices were *R*<sub>1</sub> = 0.037, *wR*<sub>2</sub> = 0.110 for *I* > 2σ(*I*) data and *R*<sub>1</sub> = 0.041, *wR*<sub>2</sub> = 0.113 for all data.<sup>4,5</sup>

**Spectrometers.** IR spectra were recorded on a Perkin-Elmer model 883 spectrometer at a resolution of 2 cm<sup>-1</sup>. FT-Raman spectra were recorded on a Bruker model 66 spectrometer equipped with an FRA-106 Raman module and a Ge-cooled detector. The resolution was 2 cm<sup>-1</sup> and the wavenumber accuracy 0.01 cm<sup>-1</sup>. The scattered radiation from the solid sample was passed through a filter module to remove the Rayleigh scattering. The power of the YAG laser was 200 mW.

**Materials.** 8-AQ was obtained from Fluka. *N*-Deut-

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erated 8-AQ was obtained after several crystallizations in  $\text{CH}_3\text{OD}$  performed in a dry-box. About 60% deuteration was achieved. Suitable crystals of 8-AQ were obtained by slow evaporation from light petroleum.

## RESULTS AND DISCUSSION

The atom numbering is shown in Figure 1. Figure 2 illustrates the intermolecular interactions in the crystal lattice. Bond lengths and bond distances are collected in Table 1. Atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

The molecule in the solid state has the amino configuration. The sum of the bond angles at the amino nitrogen is  $348.8^\circ$  and the dihedral angle between the least-squares plane of the ring and the plane of the amino group is  $38^\circ$ . The  $\text{NH}_2$  group has a higher pyramidal character than in 2-aminopyridine<sup>6</sup> or in 2-aminopyrimidine,<sup>7</sup> where the sum of the angles at the amino nitrogen is almost  $355^\circ$ . The lesser degree of  $\pi$ -conjugation in 8-AQ is also indicated by the amino-nitrogen to ring bond length of  $1.377 \text{ \AA}$ , which is higher than in 2-aminopyridine ( $1.351 \text{ \AA}$ ) or in 2-aminopyrimidine ( $1.342 \text{ \AA}$ ).

The  $\text{N}(1)\cdots\text{N}(8)$  distance of  $2.742 \text{ \AA}$ , the  $\text{N}(1)\cdots\text{H}(82)$  distance of  $2.393 \text{ \AA}$  (about  $0.3 \text{ \AA}$  shorter than the sum of the Van der Waals radii) and the  $\text{N}(1)\text{H}(82)\text{N}(8)$  angle of  $102.7^\circ$  are strong indications of the existence of an intramolecular hydrogen bond. These intramolecular  $\text{N}\cdots\text{N}$  distances are usually in the range  $2.5\text{--}2.9 \text{ \AA}$  with  $\text{NH}\cdots\text{N}$  angles between  $95$  and  $125^\circ$ .<sup>1</sup>

The results also indicate that the quinoline ring is nearly planar, the mean deviation from the plane of the ring being  $0.010 \text{ \AA}$ . The molecules are held together by weak centrosymmetrical hydrogen bonds, the  $\text{N}(8)\cdots\text{N}'(1)$  distance of  $3.314 \text{ \AA}$  being not far of the upper limit of  $3.38 \text{ \AA}$

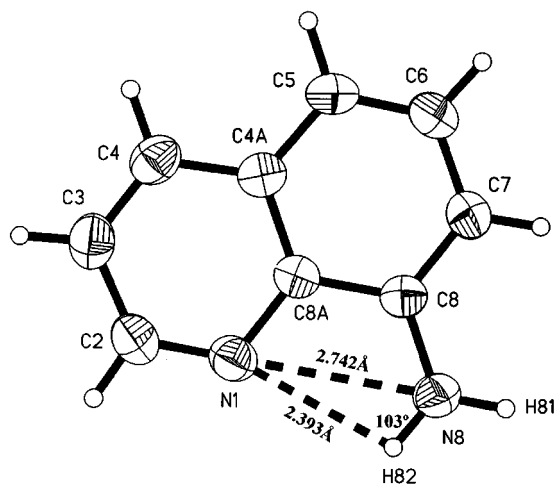


Figure 1. Atom numbering and ORTEP drawing of 8-AQ

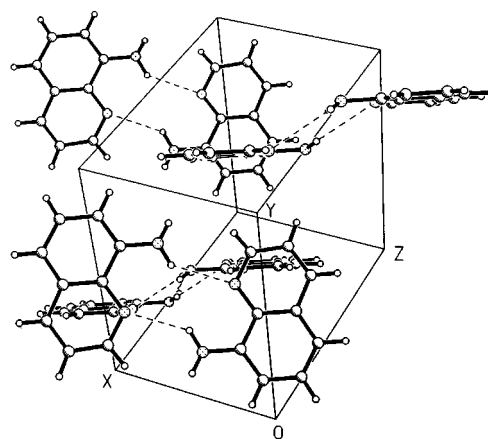


Figure 2. Packing of the 8-AQ in the unit cell showing the intermolecular hydrogen bonds

quoted in Ref. 1. The two molecules of the dimer are parallel and equivalent but they are not coplanar, the two ring planes being offset by  $1.52 \text{ \AA}$ . The other intermolecular contacts are larger than the sum of the Van der Waals radii. The second NH bond of the  $\text{NH}_2$  group remains essentially free and is not involved in hydrogen bond formation with the  $\pi$ -electrons of the aromatic ring such as in the case of 1,1'-di(amino-3,3-dimethylphenyl)cyclohexane.<sup>8</sup> In this molecular assembly, which is deficient in hydrogen-bond acceptors, the structure can be accommodated through the formation of a hydrogen bond with  $\pi$ -electrons and through a change in hybridization of the  $\text{NH}_2$  group, in agreement with the rules of Etter<sup>9</sup> for predicting hydrogen bond patterns. In the present case, the fact that one NH bond remains free can be accounted for by the rigidity of the quinoline ring and the rules of Etter<sup>9</sup> cannot be successfully applied.

Hence the  $\text{N}(8)\text{H}(82)$  group is involved in a three-center hydrogen bond, the major component being the intramolecular hydrogen bond with a distance of  $2.393 \text{ \AA}$  and the minor component being the intramolecular hydrogen bond with a distance of  $2.393 \text{ \AA}$  and the minor component being the intermolecular hydrogen bond with a distance of  $2.596 \text{ \AA}$ . In adenine derivatives, the intramolecular hydrogen bond appears invariably as the long component of the three-center hydrogen bond. In  $N^6,N^9$ -dimethyladenine,<sup>10</sup> 8-*tert*-butyladenine<sup>11</sup> and 8-ethyl-9-methyladenine dihydrate,<sup>12</sup> the intramolecular  $\text{H}\cdots\text{N}$  distances are between  $2.74$  and  $2.86 \text{ \AA}$  and the intermolecular distances between  $2.04$  and  $2.24 \text{ \AA}$ .

The IR spectra of 8-AQ and of its deuterated counterpart are shown in Figure 3. The Raman spectrum of 8-AQ is reproduced in Figure 4. Some IR data of 8-AQ are available in the literature,<sup>13</sup> but the assignment we propose in this work is different, especially for the vibrations involving the  $\text{NH}_2$  group. The Raman spectrum has not yet been described. The spectral data are summarized in Table 2.

Table 1. Bond lengths (Å), angles (°) and intermolecular contacts (Å)

N(1)—C(2)	1.314(3)	N(1)—C(8A)	1.370(2)
C(2)—C(3)	1.404(3)	C(2)—H(2)	0.95(2)
C(3)—C(4)	1.355(3)	C(3)—H(3)	0.94(2)
C(4)—C(4A)	1.413(3)	C(4)—H(4)	0.98(2)
C(4A)—C(5)	1.412(3)	C(4A)—C(8A)	1.416(3)
C(5)—C(6)	1.366(3)	C(5)—H(5)	1.00(2)
C(6)—C(7)	1.397(3)	C(6)—H(6)	0.95(2)
C(7)—C(8)	1.376(3)	C(7)—H(7)	0.96(2)
C(8)—N(8)	1.377(2)	C(8)—C(8A)	1.432(3)
N(8)—H(81)	0.92(2)	N(8)—H(82)	0.91(3)
C(2)—N(1)—C(8A)	117.0(2)	N(1)—C(2)—C(3)	124.6(2)
N(1)—C(2)—H(2)	113.9(13)	C(3)—C(2)—H(2)	121.5(13)
C(4)—C(3)—C(2)	118.7(2)	C(4)—C(3)—H(3)	123.1(14)
C(2)—C(3)—H(3)	118.2(14)	C(3)—C(4)—C(4A)	119.9(2)
C(3)—C(4)—H(4)	122.9(13)	C(4A)—C(4)—H(4)	117.2(13)
C(5)—C(4A)—C(4)	123.2(2)	C(5)—C(4A)—C(8A)	119.8(2)
C(4)—C(4A)—C(8A)	117.0(2)	C(6)—C(5)—C(4A)	119.3(2)
C(6)—C(5)—H(5)	120.6(12)	C(4A)—C(5)—H(5)	120.1(12)
C(5)—C(6)—C(7)	121.6(2)	C(5)—C(6)—H(6)	120.6(13)
C(7)—C(6)—H(6)	117.7(13)	C(8)—C(7)—C(6)	121.2(2)
C(8)—C(7)—H(7)	119.7(13)	C(6)—C(7)—H(7)	119.0(13)
N(8)—C(8)—C(7)	122.1(2)	N(8)—C(8)—C(8A)	119.4(2)
C(7)—C(8)—C(8A)	118.4(2)	N(1)—C(8A)—C(4A)	122.8(2)
N(1)—C(8A)—C(8)	117.5(2)	C(4A)—C(8A)—C(8)	119.7(2)
C(8)—N(8)—H(81)	115.8(14)	C(8)—N(8)—H(82)	117(2)
H(81)—N(8)—H(82)	116(2)		
N(1)⋯N(8) <sup>a</sup>	3.314(2)		
N(1)⋯H(82) <sup>i</sup>	2.60(3)		
N(1)⋯H(82) <sup>i</sup> —N(8) <sup>j</sup>	136(2)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $i = 1 - X, 1 - Y, -Z$ .

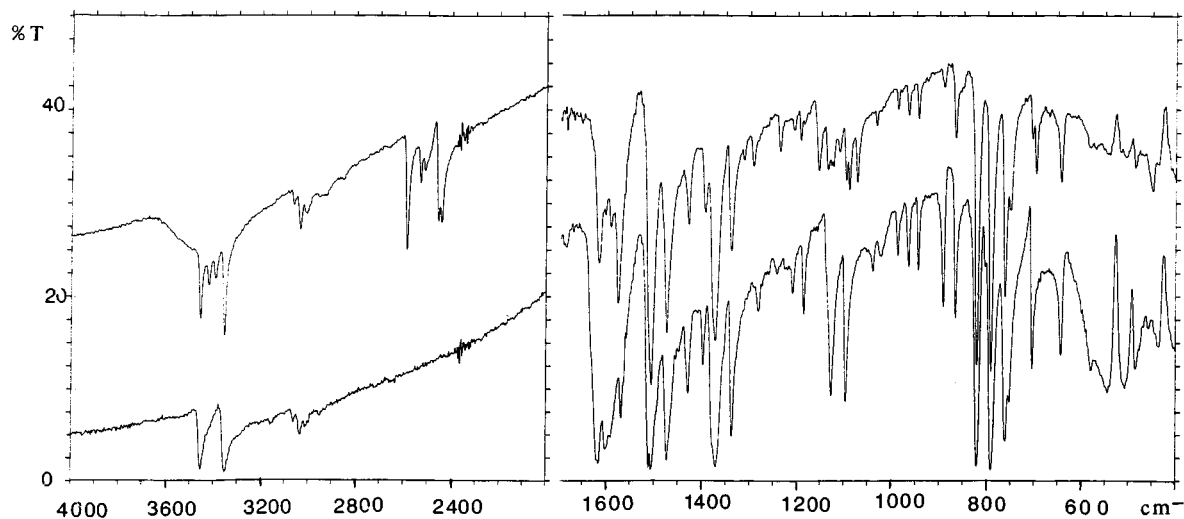


Figure 3. IR spectra (4000–400  $\text{cm}^{-1}$ ) of (A) 8-AQ  $\text{NH}_2$  and (B) A mixture of 8-AQ- $\text{NH}_2$ , 8-AQ- $\text{ND}_2$  and 8-AQ-NHD (KBr suspension)

The  $\nu(\text{NH}_2)$  vibrations, very weak in the Raman spectrum, are observed at 3454 and 3353  $\text{cm}^{-1}$  in the IR spectrum of 8-AQ- $\text{NH}_2$  and at 2584 and 2452–2438  $\text{cm}^{-1}$  in 8-AQ- $\text{ND}_2$ . This last doublet probably originates from a

Fermi resonance interaction with the  $2 \times 1237 \text{ cm}^{-1}$  level. The weakness of the intermolecular hydrogen bond is reflected by the small broadness of the  $\nu(\text{NH}_2)$  or  $\nu(\text{ND}_2)$  absorptions and by the fact that in dilute carbon tetrachlo-

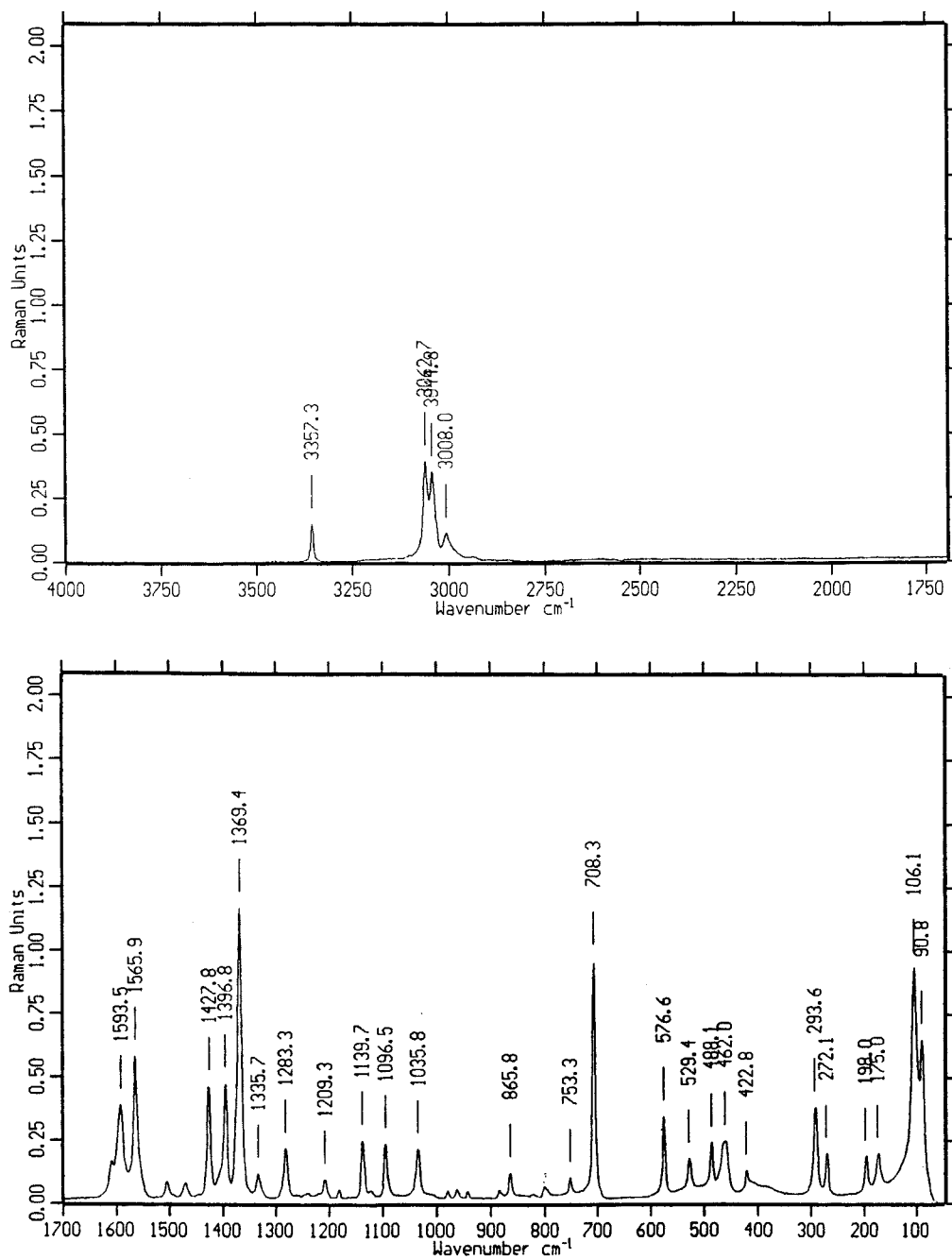


Figure 4. Raman spectrum (4000–50  $\text{cm}^{-1}$ ) of 8-AQ- $\text{NH}_2$

ride, where only monomeric species are present, the  $\nu(\text{NH}_2)$  vibrations are observed at 3502 and 3393  $\text{cm}^{-1}$  and the  $\nu(\text{ND}_2)$  vibrations at 2617 and 2493–2468  $\text{cm}^{-1}$ .<sup>3</sup> The formation of intermolecular hydrogen bonds results in small frequency shifts, about 50–60  $\text{cm}^{-1}$  for the  $\text{NH}_2$  species and about 30–40  $\text{cm}^{-1}$  for the  $\text{ND}_2$  species. The weakness of the intermolecular hydrogen bond is also reflected by the mean

value of the isotopic ratio of 1.350, which is about the same as for a free  $\text{NH}_2$  group.<sup>14</sup> The non-equivalence of the two  $\text{NH}_2(\text{NH}_2)$  bonds is clearly shown by the splitting of the  $\nu(\text{NH}(\text{D}))$  vibrations at 3417 and 3390  $\text{cm}^{-1}$  and of the  $\nu(\text{ND}(\text{H}))$  vibrations at 2527 and 2509  $\text{cm}^{-1}$  in the IR spectrum of 8-AD- $\text{ND}_2$  where residual NHD groups are present. In *o*-phenylenediamines, where intramolecular

Table 2. IR and Raman data ( $\text{cm}^{-1}$ ) for solid 8-AQ- $\text{NH}_2$  and 8-AQ- $\text{NH}_2^a$

IR (8-AQ- $\text{NH}_2$ )	IR (8-AQ- $\text{ND}_2$ )	Raman (8-AQ- $\text{NH}_2$ )	Assignment
3534 m	2586 m	3456 vvw	$\nu^{\text{as}}(\text{NH}_2, \text{ND}_2)$
—	3420 w	—	$\nu(\text{NHD})$
—	3393 w	—	$\nu(\text{NHD})$
3353 m	2453, 2440 m	3357 w	$\nu^s(\text{NH}_2, \text{ND}_2)$
—	2529 w	—	$\nu(\text{NDH})$
—	2511 w	—	$\nu(\text{NHD})$
1617 s	1616 m	1611 w	$\nu(\text{R})$
1602 s	—	—	$\delta(\text{NH}_2)$
1596 m	1591 w	1594 m	$\nu(\text{R})$
1569 m	1576 m	1566 m	$\nu(\text{R})$
1507 s	1576 m	1506 vw	$\nu(\text{R})$
1473 s	1473 s	1472 vw	$\nu(\text{R})$
1429 m	1428 m	1428 m	$\nu(\text{R})$
1398 m	1393 m	1397 m	$\nu(\text{R})$
1371 s	1372 s	1369 s	$\nu(\text{R})$
1338 s	1339 m	1336 w	$\nu(\text{R})$
—	1293 w	—	$\nu(\text{CN})$ in NHD
1283 w	1313 w	1283 w	$\nu(\text{CN})$ in $\text{NH}_2$ , $\text{ND}_2$
1244 w	1237 w	1241 vvw	$\delta(\text{CH})$
—	1155 m	—	$\delta(\text{ND}_2)$
1128 s	1136 w	1125 m	$\delta(\text{CH}) + \text{r}(\text{NH}_2, \text{ND}_2)$
—	1130 w	—	$\delta(\text{CH}) + \text{r}(\text{NDH})$
—	1089 w	—	$\delta(\text{CH}) + \text{r}(\text{NHD})$
1096 s	1073 w	1096 m	$\delta(\text{CH}) + \text{r}(\text{NH}_2, \text{ND}_2)$
1029 w	850 w	—	$\text{r}(\text{NH}_2, \text{ND}_2)$
988 m	988 w	981 vvw	$\gamma(\text{CH})$
965 m	965 w	964 vvw	$\gamma(\text{CH})$
944 m	945 w	945 vvw	$\nu(\text{R})$
891 s	891 w	886 vvw	$\nu(\text{R})$
866 s	866 m	866 w	$\nu(\text{R})$
822 vs	821 vs	823 w	$\gamma(\text{CH}) + \nu(\text{R})$
792 vs	762 s	—	$\gamma(\text{CH})$
761 s	762 s	—	$\nu(\text{R})$
708*	708 w	708 s	$\nu(\text{R})$
704 m	697 m	—	$\nu(\text{R})$
643 m	643 m	—	$\nu(\text{R})$
530 <sup>b</sup>	529 m	529 w	$\nu(\text{R})$
490 <sup>b</sup>	494 w	488 w	$\nu(\text{R})$
427 <sup>b</sup>	425 m	423 w	$\gamma(\text{R})$
		294 m	$\nu(\text{CN})$ or $\gamma(\text{R})$
		272 w	$\nu(\text{CN})$ or $\gamma(\text{R})$
		106 s	Lattice
		91 m	Lattice

<sup>a</sup> s=strong; m=medium; w=weak; v=very;  $\nu$ =stretching;  $\delta$ =in-plane deformation;  $\gamma$ =out-of-plane deformation

<sup>b</sup> Evans hole.

interactions are significant, the NHD group exhibits 'free' and 'bonded'  $\nu(\text{NHD})$  frequencies.<sup>15</sup> In 3-aminoquinoline, where the formation of an intramolecular hydrogen bond can be ruled out, the  $\nu(\text{ND}_2)$  vibrations are observed at 2587 and 2500  $\text{cm}^{-1}$  and in the partially deuterated derivative only one  $\nu(\text{ND})$  vibration is observed at 2524  $\text{cm}^{-1}$ , the average of the asymmetric and symmetric vibrations.<sup>16</sup>

The in-plane deformation ( $\delta$ ), rocking, wagging and torsion vibrations of the  $\text{NH}_2$  group in aniline are observed at 1620, 1055, 570 and 300  $\text{cm}^{-1}$ .<sup>17-19</sup> In 8-AQ- $\text{NH}_2$ , the in-plane deformation is strongly coupled with the ring vibrations of quinoline; the absorption at 1602  $\text{cm}^{-1}$  is the most sensitive to deuteration and has a predominant  $\delta(\text{NH}_2)$  character. The frequencies of the ring vibrations between 1620 and 1515  $\text{cm}^{-1}$ , strong in IR but weak in Raman, do not differ greatly from those observed in quinoline.<sup>20</sup> The  $\nu(\text{NH}_2)$  vibration observed at 1155  $\text{cm}^{-1}$  in the IR spectrum, but very weak in the Raman spectrum, is probably coupled with the  $\delta(\text{CH})$  mode; its counterpart in 8-AQ- $\text{ND}_2$  is observed with a very weak intensity. The band at 1283  $\text{cm}^{-1}$  observed in both absorption and diffusion is assigned to the  $\nu(\text{CN}_{\text{amino}})$  vibration, in agreement with Ref. 13. As in aniline,<sup>17</sup> this band is shifted upwards upon deuteration. The main component of the rocking vibration of the  $\text{NH}_2$  group is observed at 1029  $\text{cm}^{-1}$  (850  $\text{cm}^{-1}$  in 8-AQ- $\text{ND}_2$ ). This vibration is coupled with the  $\delta(\text{CH})$  vibrations and triplets arising from the interaction with the rocking modes of the  $\text{NH}_2$ ,  $\text{ND}_2$  and NHD groups are observed between 1136 and 1128  $\text{cm}^{-1}$  and between 1089 and 1073  $\text{cm}^{-1}$ . The out-of-plane vibrations  $\gamma(\text{CH})$  are not very sensitive to deuteration.

A broad band culminating at 550–525  $\text{cm}^{-1}$  is observed in the IR spectrum of 8-AQ- $\text{NH}_2$ . As in aniline derivatives,<sup>21</sup> this band is interrupted by Evans holes. In the present case, the holes are observed at 708, 530, 490 and 423  $\text{cm}^{-1}$  and are assigned to a resonance interaction with the out-of-plane deformation vibrations of the quinoline ring. Interestingly, the frequencies of the minima nearly coincide with the experimental Raman frequencies of 708, 529, 488 and 423  $\text{cm}^{-1}$ . The frequency of the wagging vibration of about 550  $\text{cm}^{-1}$  also suggests that the three-center hydrogen bond is weak. Frequencies higher than 900  $\text{cm}^{-1}$  have indeed been observed for strong  $\text{NH}\cdots\text{N}$  hydrogen bonds.<sup>22</sup>

In the low-frequency region of the Raman spectrum, two bands are observed at 106 and 91  $\text{cm}^{-1}$ . These vibrations are assigned to lattice vibrations involving the in-plane and out-of-plane vibrations of the hydrogen bond.

## CONCLUSIONS

The x-ray structure and the vibrational spectra both show the existence of a three-center hydrogen bond 8-AQ, the major component being the intramolecular hydrogen bond and the minor component being the intermolecular hydrogen bond. The weakness of the three-center hydrogen bond is reflected in the IR and Raman spectra by the frequencies

of the vibrations involving the  $\text{NH}_2$  group and by the isotopic ratio of the stretching vibrations.

In previous work,<sup>3</sup> we have shown that the thermodynamic parameters of complexes with hydroxylic proton donors are much higher for 3-AQ than for 8-AQ. For the complex between phenol and 3-AQ in carbon tetrachloride, the stability constant at 298 K is 55  $\text{mol}^{-1}$ , the enthalpy of complex formation is 34  $\text{kJ mol}^{-1}$  and the frequency shift of the  $\nu(\text{OH})$  stretching vibration is 540  $\text{cm}^{-1}$ . For the interaction involving the same proton donor and 8-AQ, these values are much lower: 8  $\text{l mol}^{-1}$ , 20  $\text{kJ mol}^{-1}$  and 375  $\text{cm}^{-1}$ , respectively. These results have been accounted for by the existence of *peri*-interaction in 8-AQ, making the lone pair of the heterocyclic nitrogen atom less available. The x-ray structure of 8-AQ reported here confirms this statement. The same effect has recently been discussed for carbonyl bases. When neither lone pair is available, the acceptor strength of the carbonyl is strongly reduced.<sup>23,24</sup>

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