

## FT-MW AND MILLIMETER WAVE SPECTROSCOPY OF PANHS: PHENANTHRIDINE, ACRIDINE, AND 1,10-PHENANTHROLINE

DON MCNAUGHTON, PETER D. GODFREY, AND RONALD D. BROWN

School of Chemistry, Monash University, Clayton, Victoria 3800, Australia; don.mcnaughton@sci.monash.edu.au

SVEN THORWIRTH

Max-Planck-Institut für Radioastronomie, Auf dem Hügel 69, 53121 Bonn, Germany

AND

JENS-UWE GRABOW

Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie und Elektrochemie,  
Lehrgebiet A Callinstraße 3A, D-30167 Hannover, Germany

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### ABSTRACT

The pure rotational spectra of phenanthridine, acridine, and 1,10-phenanthroline, small polycyclic aromatic nitrogen heterocycle molecules (PANHs), have been measured and assigned from 2 to 85 GHz. An initial spectral assignment, guided by *ab initio* molecular orbital predictions, employed broadband Stark modulated millimeter wave absorption spectroscopy of a supersonic rotationally cold molecular beam, yielding a preliminary set of rotational and centrifugal distortion constants. Subsequent spectral analysis employed Fourier transform microwave (FT-MW) spectroscopy of a supersonic rotationally cold molecular beam. The extremely high spectral resolution of the FT-MW instrument yielded improved rotational constants and centrifugal distortion constants, together with nitrogen quadrupole coupling constants, for all three species. Density functional theory (DFT) calculations at the B3LYP level of theory employing the cc-pVTZ and 6-311+G\*\* basis sets are shown to closely predict rotational constants and to be useful in predicting quadrupole coupling constants and dipole moments for such PANH species. The data presented here will be useful for deep radio astronomical searches for PANHs employing large radio telescopes.

*Subject headings:* astrochemistry — molecular data

*Online material:* machine-readable tables

### 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) were hypothesized some 20 years ago as plausible carriers responsible for the so-called unidentified infrared bands (UIRs; Leger & Puget 1984; Allamandola et al. 1985) and the diffuse interstellar bands (Leger & d'Hendecourt 1985; van der Zwet & Allamandola 1985). Since that time there have been an increasing number of laboratory and theoretical studies of this astrophysically important class of molecules and their molecular ions, with recent reviews by Allamandola & Hudgins (2003), Sarre (2006), and Duley (2006) outlining the history and present state of thinking in this area. A number of discrepancies between observational data and laboratory and theoretical studies still need to be explained, and recent work has focused on these discrepancies. Recently it has been postulated by Hudgins et al. (2005) that PAH variants containing one or more nitrogen substituents, the polycyclic aromatic nitrogen heterocycles (PANHs), may be responsible for variations in the peak position in the 6.2  $\mu\text{m}$  interstellar emission feature. There are only a small number of theoretical and laboratory studies on PANHs and their even smaller two ring relatives. Carbazole has been the subject of a microwave study (Suenram et al. 1988); recent matrix isolation infrared studies have been carried out on quinoline and phenanthridine (Bernstein et al. 2005) and a range of other selected PANHs (Mattioda et al. 2003); The structure and electronic spectra of monoazaphenanthrenes have been studied by fluorescence and theory (Deperasinska & Prochorow 2003; Prochorow et al. 2004). Unlike the PAHs, which (with the notable exception of corannulene; Lovas et al. 2005) generally have zero or low dipole moments, the PANHs have substantial dipole mo-

ments because of the polarity induced by the nitrogen substituents and hence are promising targets for rotational spectroscopic investigations in the laboratory and subsequent radio astronomical searches. Identification of PANHs in space through their rotational spectra would provide an opportunity for the observation of individual molecular carriers and another route to understanding their possible role in astrochemistry. Initial attempts to detect simple one- and two-ring aromatic nitrogen heterocycles in a number of selected astronomical sources have been unsuccessful (Charnley et al. 2005), and UV irradiation matrix isolation studies on the simple single-ring nitrogen heterocycles pyridine and s-triazine indicate that they will probably not survive in most astrophysical environments other than dense clouds (Peeters et al. 2005).

Apart from carbazole (Suenram et al. 1988) and 9-cyanoanthracene (Ohshima et al. 2004), which have structural similarities to PANHs, rotational spectroscopic studies in the laboratory have mainly been carried out to date on the relatively simple aromatic nitrogen heterocycles, pyridine (Ye et al. 2005), pyrimidine (Blackman et al. 1970; Kisiel et al. 1999), quinoline, and isoquinoline (Kisiel et al. 2003), mainly because their intrinsic vapor pressures allow for relatively simple experimental conditions. The larger PANHs, partly because they are solids at room temperature, have until recently not been experimentally studied in the gas phase. Recently, we presented a rotational analysis in the millimeter-wave region of phenanthridine, a monoaza variant of phenanthrene (McNaughton et al. 2007). In the present paper we give a full account of our study of PANHs: in addition to an extended spectroscopic analysis of phenanthridine into the microwave region, where  $^{14}\text{N}$  quadrupole coupling constants are accessible from the

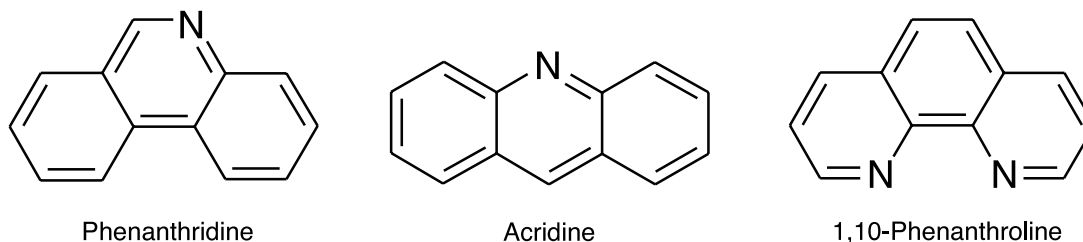


FIG. 1.—Molecular structures of phenanthridine (*left*), acridine (*center*), and 1,10 phenanthroline (*right*).

data, we have recorded and analyzed the rotational spectra of acridine (a monoaza variant of anthracene) and 1,10 phenanthroline (a diaza derivative of phenanthrene; Fig. 1), two PANH molecules of similar size and vapor pressure to phenanthridine. These rotational analyses provide molecular constants with which to predict the rotational spectra and quadrupole hyperfine structure accurately throughout the microwave range, i.e., in those regions of the spectrum amenable to large radio telescopes.

## 2. THEORY AND EXPERIMENT

### 2.1. Millimeter-Wave Spectroscopy

All millimeter-wave spectra (45–95 GHz) were recorded with a Stark-modulated free-jet spectrometer described in Brown et al. (1988), but modified to replace the original klystron sources with solid-state oscillators, and with the frequency range extended to an upper limit of around 100 GHz. A 33 kHz square-wave Stark modulation system was used to supply parallel-plate electrodes separated by  $\sim 3.5$  cm. Phenanthridine (98%, Sigma-Aldrich), acridine (97%, Sigma-Aldrich) and 1,10 phenanthroline (>99%, Sigma-Aldrich) were vaporized at between 140°C and 160°C in a stream of argon at a pressure of  $\sim 0.3$  atm. The gaseous sample was introduced into the Stark field through a 350  $\mu\text{m}$  diameter pinhole nozzle held 10°C above the vaporization temperature. Under these conditions the post-expansion rotational temperature was  $\sim 10$  K, and no evidence of thermal decomposition was observed. Electric fields of up to  $1600 \text{ V cm}^{-1}$  were possible, and the highest sustainable voltage was used in the scans to maximize the degree of Stark modulation. The microwave spectrum was first investigated by carrying out an extended spectral scan over a wide frequency range (48–72 GHz) using a strip chart with detected lines subsequently digitally acquired by integration of repetitively averaged narrow band scans. Line center frequencies were measured by least-squares fitting a Lorentzian function to each line profile. The typical full width half-height of the transitions was 300 kHz, leading to experimental line uncertainties of 20–60 kHz.

### 2.2. FT-MW Spectroscopy

The rotational transitions in the centimeter-wave region were obtained using a high-resolution Fourier transform microwave (FT-MW) spectrometer—a pulsed-supersonic jet, Fabry-Pérot type resonator spectrometer (Balle & Flygare 1981). The spectrometer implements an automated (Andresen et al. 1990), broadband (2–26.5 GHz) setup utilizing a coaxially oriented beam-resonator arrangement (COBRA; Grabow et al. 1996), i.e., the molecular jet expands coaxially to the axis of the near-confocal spherical reflectors. The principal advantage of the longer transit time of the molecular jet in the coaxial arrangement is that it results in long-lasting signals (Grabow & Stahl 1990) and consequently very narrow line widths of about 1.5 kHz (HWHH), with neon as the

carrier gas. This system yields a resolving power of about 5 kHz while achieving experimental uncertainties of less than 500 Hz for unblended lines. All frequency measurements were referenced to a global positioning system (GPS) controlled frequency standard. To obtain sufficient vapor pressure to record the rotational spectrum, the sample was heated in a reservoir nozzle with 1.5 mm orifice installed in the rear of one of the reflectors of the Fabry-Pérot resonator (Lovas et al. 2005). Most measurements were carried out at a nozzle temperature between 120°C and 140°C at a backing pressure near 100 kPa, a pulse repetition rate of 20 Hz, and with neon as the carrier gas. Using these conditions, rotational temperatures of less than 2 K are typically obtained.

In total between the two techniques, 290 lines of phenanthridine, 163 of acridine, and 246 lines of phenanthroline were assigned and fitted.

### 2.3. Theoretical Predictions

Initial rotational constants, quadrupole coupling constants, dipole moments, and harmonic vibrational frequencies of both molecules were predicted at the B3LYP level of theory employing the cc-pVTZ and 6-311+G\*\* basis sets as implemented in GAUSSIAN 03 (Frisch et al. 2003). The level of theory was chosen for two reasons. First, recent *ab initio* calculations on aromatic hydrocarbons using electron correlation at a number of basis sets have shown unexpected nonplanar geometries, whereas DFT calculations and the basis used here have been shown to not give these spurious results (Moran et al. 2006), and hence are appropriate for the study of the polycyclic hydrocarbons in this work. Second, B3LYP/cc-pVTZ calculations have been employed successfully in recent rotational spectroscopy studies of selected PAHs (Thorwirth et al. 2006, 2007) and B3LYP/6-311+G\*\* calculations predicted the rotational constants of phenanthridine to better than 0.25% in our previous study. Planarity was not assumed in the latter work. For the prediction of centrifugal distortion constants, we also used the ACES II program (Stanton et al. 1992).<sup>1</sup>

## 3. RESULTS AND DISCUSSION

The advantage of the millimeter-wave absorption spectrometer system is its broad scanning range, which allows for a rapid search for spectral lines, while the centimeter-wave FT-MW instrument with its short scan range has the advantage of much higher sensitivity and spectral resolution. Hence, the initial assignments were carried out using the absorption instrument, and the results were used to predict low-frequency transitions for the FT-MW measurements. The results of B3LYP/6-311+G\*\* and B3LYP/cc-pVTZ calculations are given in Tables 1 and 2, together with experimental results. As can be seen, for phenanthridine the

<sup>1</sup> For current version see <http://www.aces2.de>.

TABLE 1  
 SPECTROSCOPIC CONSTANTS OF PHENANTHRIDINE (IN MHz)

Constant	B3LYP/cc-pVTZ <sup>a</sup>	B3LYP/6-311G** (SCF/DZP) <sup>b</sup>	Experimental (McNaughton 2007)	Experimental (This Work)
<i>A</i> .....	1656.1	1647.2	1642.45814(39)	1642.457218(32)
<i>B</i> .....	559.4	556.7	557.73024(66)	557.7346992(224)
<i>C</i> .....	418.1	416.6	416.51092(75)	416.5095420(174)
<i>D<sub>J</sub></i> × 10 <sup>6</sup> .....		(2.96)	3.17(22)	3.3318(214)
<i>D<sub>JK</sub></i> × 10 <sup>6</sup> .....		(0.19)		...
<i>D<sub>K</sub></i> × 10 <sup>6</sup> .....		(47.9)	55.34(59)	54.410(141)
<i>d</i> <sub>1</sub> × 10 <sup>5</sup> .....		(−0.92)		−1.0403(114)
<i>d</i> <sub>2</sub> × 10 <sup>5</sup> .....		(−0.124)		−0.1424(299)
<i>χ<sub>aa</sub></i> .....	−0.54	−0.43		−0.6054(89)
<i>χ<sub>bb</sub></i> .....	−2.18	−2.22		−2.5829(54)
<i>χ<sub>cc</sub></i> .....	2.72	2.65		...
<i>χ<sub>ab</sub></i> .....	2.40	2.65		3.046(293)
<i>Δ</i> <sup>c</sup> .....	−0.413			−0.4576
wrms <sup>d</sup> .....				0.852

<sup>a</sup> McNaughton et al. (2007).<sup>b</sup> The DFT predicted centrifugal distortion constants are not included.<sup>c</sup> Inertial defect,  $\Delta = I_c - I_b - I_a$ , in units of u.<sup>d</sup> Weighted rms, dimensionless.

predicted rotational constants are remarkably close to the experimentally derived constants, and we approached the initial assignment for acridine and 1,10 phenanthroline expecting similar quality predictions and small centrifugal distortion effects, as observed in phenanthridine. An initial assignment for each molecule was easily achieved by comparing a predicted stick spectrum (50–54 GHz) with the observed chart recorder output, with the presence of predicted closely spaced asymmetry doublets confirming the assignment. Following a rigid rotor fit, further lines in the frequency region 48–85 GHz were well predicted, and further assignments were relatively straightforward. In this way we produced a fit for all three molecules capable of predicting the FT-MW spectra. Tables 1 and 2 also contain the eventual rotational constants from the final fit, showing that the rotational constants for all molecules are extremely well predicted with the ab initio predictions within 0.25% at the B3LYP/6-311G\*\* level

of theory, while the centrifugal distortion constants for all but phenanthridine were within 10% of the predictions. Given that the comparison is between theoretical equilibrium rotational constants and ground-state constants, the level of agreement is excellent. Because of the extremely poor correlation of the Gaussian calculated DFT centrifugal distortion constants for phenanthridine, we also optimized all three structures using ACESII at the SCF/DZP and found that the centrifugal distortion constants (given in Tables 1 and 2) are well predicted at this level of theory for all three molecules. This gives us confidence in our assignment, but the origin of the discrepancy in the DFT calculation for phenanthridine remains uncertain at present.

Transition frequencies and profiles of lines in the bandwidth of the FT-MW system were calculated from the fits to the millimeter-wave data and DFT-predicted quadrupole coupling constants. The lines were generally found to be very close to the

 TABLE 2  
 SPECTROSCOPIC CONSTANTS OF ACRIDINE AND PHENANTHROLINE (IN MHz)

CONSTANT	ACRIDINE			PHENANTHROLINE		
	B3LYP/cc-pVTZ	B3LYP/6-311G** (SCF/DZP)	Experimental	B3LYP/cc-pVTZ	B3LYP/6-311G** (SCF/DZP)	Experimental
<i>A</i> .....	2171.4	2159.7	2154.360021(57)	1633.5	1625.0	1619.961880(41)
<i>B</i> .....	468.4	466.1	466.574967(27)	582.6	580.0	581.495582(26)
<i>C</i> .....	385.3	383.4	383.643020(21)	429.5	427.5	428.058988(23)
<i>D<sub>J</sub></i> × 10 <sup>6</sup> .....		1.774 (1.64)	1.869(26)		3.672 (3.38)	3.823(50)
<i>D<sub>JK</sub></i> × 10 <sup>6</sup> .....		7.382 (6.52)	7.55(20)		−0.66(−0.63)	−0.40(21)
<i>D<sub>K</sub></i> × 10 <sup>6</sup> .....		64.50 (57.64)	62.20(73)		48.55 (43.8)	48.25(29)
<i>d</i> <sub>1</sub> × 10 <sup>6</sup> .....		−0.365 (0.336)	−0.366(11)		−1.185 (1.09)	−1.205(17)
<i>d</i> <sub>2</sub> × 10 <sup>6</sup> .....		−0.052 (0.047)	−0.0561(35)		−1.600 (1.47)	−1.726(68)
<i>χ<sub>aa</sub></i> .....	1.27		1.5754(52)	−0.32	−0.21	−0.3503(40)
<i>χ<sub>bb</sub></i> .....	−3.69		−4.4662(24)	−2.63	−2.68	−3.1091(21)
<i>χ<sub>cc</sub></i> .....	2.42		...	2.95	2.89	...
<i>χ<sub>ab</sub></i> .....	...		...	−2.44		
<i>μ<sub>b</sub>(D)</i> .....	1.88	2.02		3.17	3.40	
<i>Δ</i> <sup>a</sup> .....	−0.383		−0.4363	−0.396		−0.4423
wrms <sup>b</sup> .....			0.430			0.748

<sup>a</sup> Inertial defect,  $\Delta = I_c - I_b - I_a$ , in units of u.<sup>b</sup> Weighted rms, dimensionless.

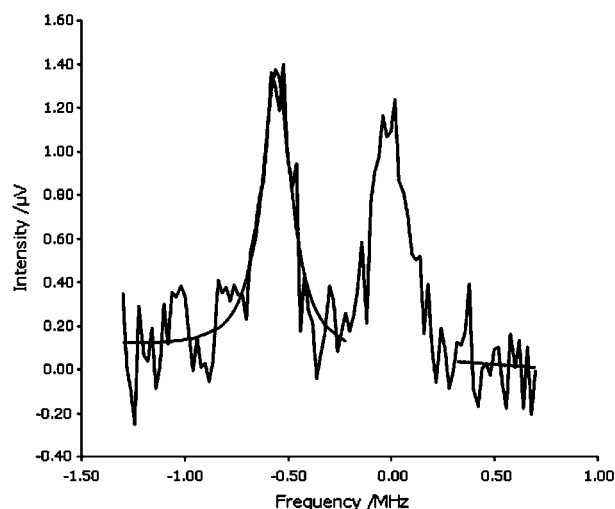


FIG. 2.— Acridine asymmetry doublet  $29_{9,21}-28_{8,20}$  53932.45 MHz;  $29_{9,20}-28_{8,21}$  53932.98 MHz, showing four co-added scans; Stark voltage is  $\pm 2500$  V.

predictions. Finally, all lines for each molecule were fitted to Watson's symmetric rotor Hamiltonian using the SPFIT program of Pickett (1991), and the resulting constants are given in Tables 1 and 2. Almost full sets of quartic centrifugal distortion constants were obtained for all three molecules investigated here (Tables 1 and 2), with the very small predicted  $D_{JK}$  values not determined for phenanthridine and not well determined for phenanthroline. For phenanthridine, the set of lines measured now consists of  $a$  and  $b$  type rotational lines, yielding a significantly improved overall fit over the previous analysis (McNaughton et al. 2007), and for the  $C_{2v}$  molecules acridine and 1,10-phenanthroline, all of the transitions observed are  $b$  type. A typical millimeter-wave spectrum is shown in Figure 2, with the lower member of an acridine asymmetry doublet,  $29_{9,21}-28_{8,20}$  fitted to a Lorentzian band of line width 170 kHz. The observed transitions for all three species, along with experimental transition frequencies, are listed in the Appendix, Tables 4, 5, and 6.

It has not been possible to measure dipole moments in our millimeter-wave experimental apparatus, but the observed intensities of the transitions of phenanthroline were much larger than for the other two molecules, correlating well with the larger predicted dipole moments. Experimental and theoretical dipole moments of selected small PANHs and other similar species are listed in Table 3, where it can be seen that B3LYP/6-311+G\*\* calculations consistently overestimate the dipole moment components, while the B3LYP/cc-pVTZ calculations are very close

to the experimental values (see also Thorwirth et al. 2004). Given these predictions, one might expect the B3LYP/cc-pVTZ dipole moment calculations in Tables 1 and 2 to provide reasonable estimates.

FT-MW spectroscopy permitted observation of hyperfine structure (hfs) from the presence of  $^{14}\text{N}$  nuclei in all three molecules. The initial assignment of hfs was guided by estimates of quadrupole coupling constants from B3LYP/cc-pVTZ calculations. As can be seen from Tables 1 and 2, generally good agreement (of better than 25%) is observed between the calculated and experimentally obtained values. In the case of phenanthridine, the lines measured were such that the complete principal nuclear quadrupole tensor could be determined (see Table 1). Taking into account flipping of the principal inertial axes  $a$  and  $b$  between monocyclic pyridine and acridine investigated here, direct comparison of the respective quadrupole coupling constants is possible. Indeed, the quadrupole coupling constant pairs for acridine [ $\chi_{aa} = 1.575(5)$  MHz,  $\chi_{bb} = -4.466(2)$  MHz; Table 2] and pyridine [ $\chi_{aa} = -4.908(3)$  MHz,  $\chi_{bb} = 1.434(3)$  MHz; Heineking et al. 1986] are quite similar, indicating that the  $^{14}\text{N}$  nuclei share similar electronic environments in the two molecules. In addition to the  $\chi_{aa}$ ,  $\chi_{bb}$  correspondence in acridine and pyridine, the  $\chi_{cc}$  coupling constants, which are proportional to the field gradient perpendicular to the aromatic plane, show rather similar values for all three PANHs. 1,10-phenanthroline is the only molecule studied here containing two nitrogen atoms, and hence shows rather complex hfs structure. However, due to the high resolution of the FT-MW technique and rather reliable predictions, assignment was easily facilitated. Figure 3 shows the complex hyperfine structure of the  $14_{2,12}-13_{3,11}$  transition of 1,10-phenanthroline. Owing to the  $C_{2v}$  symmetry of the molecule, the quadrupole coupling constants for both nuclei are identical, and we have used the coupling scheme  $F_1 = J + I$ ,  $F = F_1 + I$ . As can be seen from Tables 1 and 2, the diagonal quadrupole coupling constants have been determined to about 1% and better for all three molecules, and  $\chi_{ab}$  in phenanthridine has been determined to at least 10%. For 1,10-phenanthroline,  $\chi_{ab}$  could not be determined experimentally from the present data set. The theoretical value at the B3LYP/cc-pVTZ level of theory is  $\chi_{ab} = -2.44$  MHz.

The values for the inertial defects ( $\Delta = I_c^v + I_b^v - I_a^v$ ) of the three PANHs given in Tables 1 and 2 are all large, negative, and comparable in magnitude. The planar moments (Kraitchman 1953)  $P_{gg} = -\Delta/2$ , calculated as  $2P_{gg}^v = I_{g'}^v + I_{g''}^v - I_g^v = 2P_{gg}^e - \Delta_g^v$ , can be related to the vibrational dynamics of a molecule. In our case, with  $g = c$ ,  $g' = a$ ,  $g'' = b$ , and  $v = 0$ , we get the planar moment  $P_{cc}$  with respect to the  $ab$ -plane of the principal inertia axes systems of the oblate rotors in their vibrational ground state:  $2P_{cc}^0 = I_a^0 + I_b^0 - I_c^0 = 2P_{cc}^e - \Delta_c^0$ . From ab initio calculations

TABLE 3  
DIPOLE MOMENTS OF PANHs AND RELATED SPECIES

Species	$\mu$	B3LYP/6-311+G**	B3LYP/cc-pVTZ	Experimental
Quinoline <sup>a</sup> .....	$\mu_a$	0.2365	0.2113	0.1435(19)
	$\mu_b$	2.1567	2.0033	2.0146(17)
Isoquinoline <sup>a</sup> .....	$\mu_a$	2.535	2.3603	2.3602(21)
	$\mu_b$	0.9763	0.8939	0.9051(14)
9 Cyanoanthracene <sup>b</sup> .....	$\mu_a$	4.7712		4.406(7)
Pyrimidine <sup>c</sup> .....	$\mu_b$	2.4460	2.2793	2.334(10)

<sup>a</sup> Experimental values from Kisiel et al. (2003).

<sup>b</sup> Experimental values from Ohshima et al. (2004).

<sup>c</sup> Experimental values from Blackman et al. (1970).

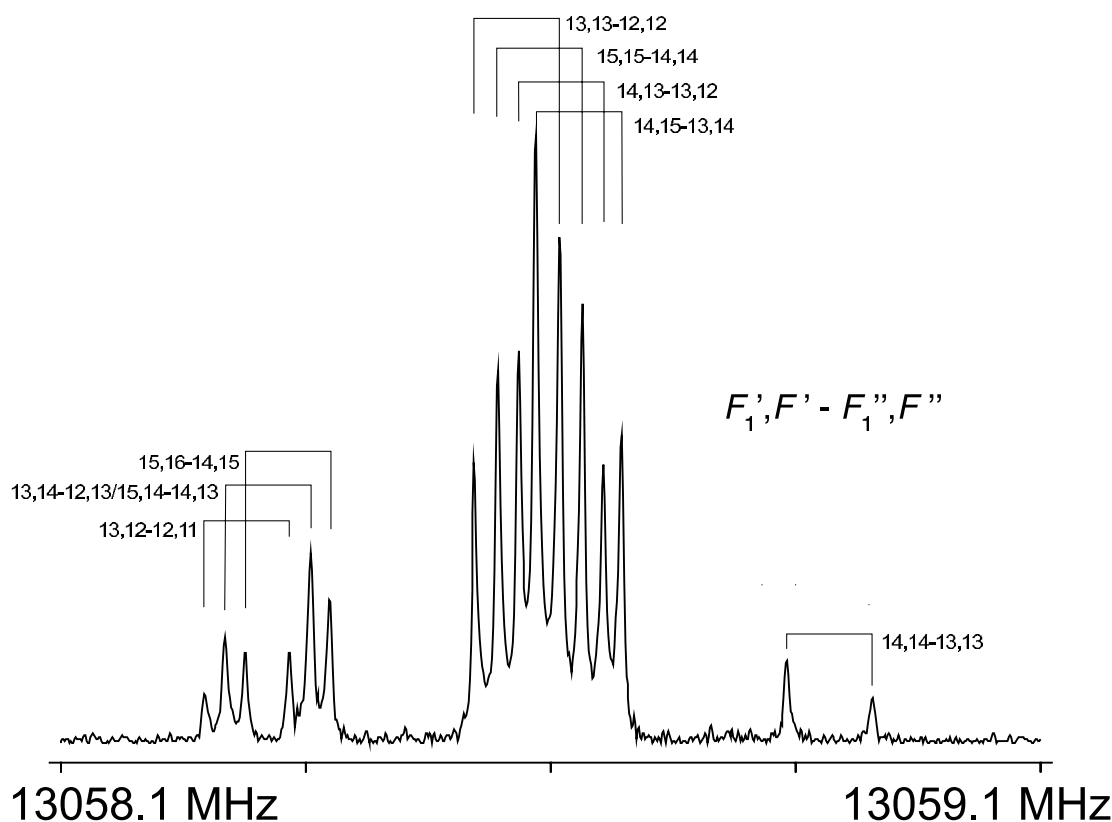


FIG. 3.—The  $14_{2,12} - 13_{3,11}$  transition of 1,10-phenanthroline.

we can estimate the equilibrium planar moment  $P_c^e$ , and thus the so-called pseudo inertial defect  $\Delta_c^0$  can be determined. It gives a measure for the magnitude of molecular vibrations, and indicates significant out-of-plane vibrations if  $\Delta_c^0$  takes on negative values. Assuming a vanishing equilibrium planar moment  $P_c^e$ , as supported by our ab initio calculations (B3LYP/6-311G\*\*), which did not assume planarity,  $P_{cc}^0 = -\Delta/2$  becomes  $-\Delta_c^0/2$ . We have already justified the large  $-\Delta$  value for phenanthridine in our previous work (McNaughton et al. 2007) as being due to the presence of a number of low-frequency out-of-plane vibrational modes, and the same arguments apply to acridine and phenanthroline as well. All three molecules have similar low frequencies for the out-of-plane modes, with one particularly low-frequency mode that contributes most to the large negative *ve* inertial defect. Tables 1 and 2 also contain predicted values for the inertial defects, calculated from equation (10) of Oka (1995) using the B3LYP/6-311+G\*\* predicted values for the harmonic out-of-plane frequencies and Coriolis coupling constants. It can be seen that these predictions are within 10% of the experimentally determined values and follow the same trends in magnitude. The only comparable large molecule for which an experimental inertial defect is available is 9 cyanoanthracene, with  $\Delta = -0.401$  u (Ohshima et al. 2004), compared with a B3LYP/6-311+G\*\* predicted value of  $-0.358$  u.

#### 4. CONCLUSIONS

The gas-phase rotational spectra of three selected PANHs have been observed. The study of phenanthridine has been extended into the FT-MW regime, and full analyses of two further three-ring PANHs, acridine and 1,10 phenanthroline, have been measured for the first time. The resulting rotational, centrifugal,

and quadrupole coupling constants given in Tables 1 and 2 are of very high accuracy and provide useful transition frequencies for deep radio astronomical searches for these species in space. The inclusion of quadrupole coupling constants in the present study provides additional data with which to provide more rigorous proof of identity in any interstellar search.

The results of this investigation and our previous study on phenanthridine indicate that other PANH species with vapor pressures and sizes similar to the molecules studied here, and probably also tetracyclic systems such as the ones in the work of Mattioda et al. (2003), are amenable to be studied by free-jet or pulsed-jet microwave absorption spectroscopy. Such studies require grams rather than milligrams of material, and will depend on the availability of the species in sufficient quantity for spectral assignment. Larger PANH molecules, however, have even lower vapor pressures and will probably require a different experimental approach for vaporization. In addition, a different spectral region for optimal detection and measurement is required, because of the much smaller rotational constants for such large molecules. A combination of laser ablation and FT-MW spectroscopy as introduced by Suenram et al. (1990) and adapted for COBRA by Walker & Gerry (1993) would presumably be the best option for such molecules.

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APPENDIX: EXPERIMENTAL ROTATIONAL TRANSITIONS

Tables 4, 5, and 6 list experimental rotational transitions for phenanthridine, phenanthroline, and acridine, respectively. The full tables are available in the online *Journal*.

TABLE 4  
PHENANTHRIDINE EXPERIMENTAL ROTATIONAL TRANSITIONS

$J'$	$K'_a$	$K'_c$	$F'$	$J''$	$K''_a$	$K''_c$	$F''$	Exp. Frequency	Diff.	Exp. Error
22	12	11	22	21	11	10	21	48021.75000	0.00948	0.03000
22	12	10	22	21	11	11	21	48021.75000	0.00920	0.03000
15	15	0	15	14	14	1	14	48119.82000	−0.00616	0.03000
15	15	1	15	14	14	0	14	48119.82000	−0.00616	0.03000
20	13	7	20	19	12	8	19	48392.05000	−0.02698	0.03000
20	13	8	20	19	12	7	19	48392.05000	−0.02698	0.03000
30	9	21	30	29	8	22	29	48480.86000	−0.00892	0.02000
25	11	15	25	24	10	14	24	48570.98000	0.04441	0.03000
25	11	14	25	24	10	15	24	48570.98000	−0.11635	0.03000

NOTE.—Table 4 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

TABLE 5  
PHENANTHROLINE EXPERIMENTAL ROTATIONAL TRANSITIONS

$J'$	$K'_a$	$K'_c$	$F'_1$	$F'$	$J''$	$K''_a$	$K''_c$	$F''_1$	$F''$	Exp. Frequency	Diff.	Exp. Error
20	13	7	20	20	19	12	8	19	19	48099.92000	−0.05314	0.02000
20	13	8	20	20	19	12	7	19	19	48099.92000	−0.05314	0.02000
27	10	18	27	27	26	9	17	26	26	48169.24000	−0.01508	0.03000
27	10	17	27	27	26	9	18	26	26	48205.78000	0.00846	0.03000
18	14	4	18	18	17	13	5	17	17	48303.47000	−0.02854	0.02000
18	14	5	18	18	17	13	4	17	17	48303.47000	−0.02854	0.02000
16	15	1	16	16	15	14	2	15	15	48500.46000	0.01906	0.02000
16	15	2	16	16	15	14	1	15	15	48500.46000	0.01906	0.02000
25	11	15	25	25	24	10	14	24	24	48598.47000	0.01421	0.02000
25	11	14	25	25	24	10	15	24	24	48598.96000	0.00494	0.02000

NOTE.—Table 5 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

TABLE 6  
ACRIDINE EXPERIMENTAL ROTATIONAL TRANSITIONS

$J'$	$K'_a$	$K'_c$	$F'$	$J''$	$K''_a$	$K''_c$	$F''$	Exp. Frequency	Diff.	Exp. Error
1	1	1	1	0	0	0	1	2536.88635	−0.00038	0.00200
1	1	1	2	0	0	0	1	2538.22747	0.00114	0.00200
1	1	1	0	0	0	0	1	2540.23635	−0.00006	0.00200
18	2	17	17	18	1	18	17	12335.19188	0.00075	0.00150
18	2	17	19	18	1	18	19	12335.25873	−0.00067	0.00150
18	2	17	18	18	1	18	18	12336.48676	0.00016	0.00100
11	2	10	11	10	1	9	10	12355.75104	−0.00030	0.00100
11	2	10	12	10	1	9	11	12356.89698	−0.00001	0.00100
11	2	10	10	10	1	9	9	12357.01445	−0.00013	0.00100

NOTE.—Table 6 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

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