

Millimetre wave spectroscopy of PANHs: phenanthridine

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The pure rotational spectrum of phenanthridine (C₁₃H₉N), a small polycyclic aromatic nitrogen heterocycle (PANH), has been measured from 48 to 85 GHz employing Stark modulated millimetre wave absorption spectroscopy of a supersonic rotationally cold molecular beam. Initial survey search scans were guided by rotational constants obtained through quantum chemical calculations performed at the B3LYP/cc-pVTZ level of theory. Close agreement—to well within 1%—is found between the calculated equilibrium and experimentally derived ground state rotational constants. From the moments of inertia a substantial negative inertial defect of $\Delta = -0.4688(44)$ amu Å² is obtained which can be explained by the presence of several energetically low-lying out-of-plane vibrational modes. Corresponding density functional theory calculations of harmonic fundamental frequencies indeed yield four such low frequency modes with values as low as 96 cm⁻¹. The data presented here will also be useful for deep radio astronomical searches for PANHs employing large radio telescopes.

I. Introduction

Since the hypothesis over 20 years ago that polycyclic aromatic hydrocarbons (PAHs) might be carriers responsible for the so-called unidentified infrared bands (UIRs)^{1,2} and the diffuse interstellar bands,^{3,4} there have been a large number of laboratory and theoretical studies of this important class of molecules. Recent reviews by Allamandola and Hudgins⁵ and Sarre⁶ chart the history and present thinking in this area and point out some of the discrepancies that exist between observational data and laboratory and theoretical studies. Recently it has been postulated that variations in peak positions in the 6.2 μm interstellar emission feature are due to polycyclic aromatic nitrogen heterocycles (PANHs), PAH variants that contain one or more nitrogen substituents.⁷ Apart from the calculations in ref. 7 detailed laboratory and theoretical studies of these species are sparse with a microwave study of carbazole,⁸ recent matrix isolation infrared works on quinoline and phenanthridine⁹ and a range of other selected PANHs¹⁰ together with theoretical and fluorescence studies on the structure and electronic spectra of monoazaphenanthrenes.^{11,12} Many of these PANHs have substantial dipole moments, due to the polarity induced by the nitrogen substituents and so they are promising targets for rotational spectroscopic investigations in the laboratory and subsequent radio astronomical searches. First attempts to detect simple aromatic nitrogen heterocycles in a number of selected astronomical sources have been unsuccessful.¹³ Identification of PANHs in space through their rotational spectra would provide a means for the observation of individual molecular carriers and another route into understanding their possible role in astrochemistry.

To date, apart from carbazole,⁸ rotational spectroscopy studies in the laboratory have been carried out for relatively simple aromatic nitrogen heterocycles only, such as pyridine, quinoline and isoquinoline,^{14,15} primarily because of the ease of obtaining these molecules in the vapour phase. The larger PANHs are solids at room temperature and provide a greater experimental challenge. We present here a rotational analysis of phenanthridine, a monoaza variant of phenanthrene (Fig. 1), which represents the rotational spectroscopic characterization of the largest PANH so far. The present investigation provides the molecular constants necessary to predict the rotational spectrum accurately throughout the microwave range, *i.e.* in those regions of the spectrum amenable to large radio telescopes.

II. Experimental and theoretical methods

Initial searches for rotational transitions of phenanthridine were based on quantum chemical calculations of rotational constants, dipole moment components and nuclear quadrupole coupling constants of nitrogen. The standard program package GAUSSIAN 03¹⁶ was used along with the density functional theory (DFT) variant B3LYP¹⁷ and the correlation consistent polarized valence basis set cc-pVTZ,¹⁸ an approach recently employed successfully in the microwave investigation of several polar PAHs.¹⁹ Further calculations at the B3LYP/6-311+G** level of theory were carried out to determine harmonic vibrational frequencies. It may be noted here that recent *ab initio* calculations on aromatic hydrocarbons using

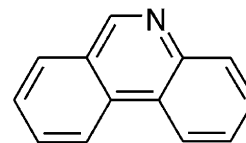


Fig. 1 Molecular structure of phenanthridine.

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electron correlation at a number of basis sets have shown unexpected non planar geometries.²⁰ DFT calculations and the cc-pVTZ basis have been shown to not give these spurious results and hence are appropriate for the study of the polycyclic hydrocarbons in this work. Accordingly, planarity was assumed during optimization of the molecular structure.

Our Stark-modulated free-jet spectrometer used for the millimetre-wave studies has been previously described²¹ but was modified to replace klystrons with solid-state oscillators, with the coverage being extended to an upper frequency limit of around 100 GHz. The 33 kHz square wave Stark modulation system employed parallel-plate electrodes with a separation of *ca.* 3.5 cm. Phenanthridine (98%, Sigma-Aldrich) was vaporized at 150 °C in a stream of argon at a pressure of ~ 0.3 atm. The gaseous sample was introduced into the Stark field through a 350 μm diameter nozzle held at 160 °C. Under these conditions, no evidence of thermal decomposition was observed and the post-expansion rotational temperature was *ca.* 10 K. Stark modulation with electric fields up to 1600 V cm^{-1} was possible and the highest sustainable voltage was used in the scans to maximise the degree of modulation. The microwave absorption spectrum was first investigated *via* an extended spectral search scan over a wide frequency range (48–72 GHz). In these strip chart recorded wide searches the sensitivity limit was *ca.* 10% of the strongest line detected. Once located *via* the wide search scan, each detected line was digitally acquired *via* repetitively averaged narrow band scans, and line frequencies measured by least-squares fitting of a Lorentzian function to each line profile. Typical full width half height of the transitions was 300 kHz leading to experimental line uncertainties of 20 to 60 kHz. In total, 116 lines (overlapping asymmetry doublets only counted once) were fitted to a Watson-type Hamiltonian using Pickett's program SPFIT.²²

III. Results and discussion

For the PAH molecules acenaphthene ($\text{C}_{12}\text{H}_{10}$), acenaphthylene (C_{12}H_8) and fluorene ($\text{C}_{13}\text{H}_{10}$), which are similar in size to phenanthridine, theoretical B3LYP/cc-pVTZ predictions proved to be useful as a starting point for spectral searches and proved to agree with the experimental constants within 1%.¹⁹ Corresponding quantum chemical calculations were carried out on phenanthridine here and the results are shown in Table 1. The eventual comparison of rotational constants with experiments is again within 1%, whilst the dipole moment predictions are greater than 1D for both μ_a and μ_b and much greater than the dipole moments of the polar PAH species of similar size and shape, indicating that they are a good prospect for laboratory rotational spectroscopy and a better prospect for astronomical detection if present in similar densities to PAHs. We estimate the dipole moment calculation to be accurate within 10%.²³ As seen from Table 1 the B3LYP/6-311G** calculated rotational constants match the experimental rotational constants extremely closely indicating that this level of theory may be more than adequate for the prediction of rotational constants of this kind of species without resorting to scaling.

Phenanthridine is a prolate asymmetric top molecule (Ray's asymmetry parameter $\kappa = (2B - A - C)/(A - C) = -0.77$

Table 1 Rotational constants, ^{14}N nuclear quadrupole coupling constants (MHz) and dipole moment components (D) of phenanthridine

Constant	B3LYP/cc-pVTZ	B3LYP/6-311G**	Observed
A^a	1656.1	1647.2	1642.5
B^a	559.4	556.7	557.6
C^a	418.1	416.6	416.6
χ_{aa}	-0.54	—	—
χ_{bb}	-2.18	—	—
χ_{cc}	2.72	—	—
μ_a	1.37	1.43	—
μ_b	1.84	1.97	—

^a Quantum chemical calculations give A_e , B_e , C_e whereas experimental values correspond to A_0 , B_0 , and C_0 , respectively.

where at first glance there are few patterns in the spectrum to assist assignment. For all but low J and K transitions however even such asymmetric molecules have patterns of approximately equally spaced transitions that can easily be discerned in high resolution infrared bands using computer techniques based on the Loomis-Wood approach. In our laboratory we have successfully used this technique to assign vibration-rotation structure for molecules with comparable asymmetry, such as 1,1-difluoroethane, HFC 152a ($\kappa = -0.75$).²⁴ We employed a similar approach to obtain initial assignments in the present study from measurements in the V band region (48–72 GHz). The individual branches located were essentially fitted to a high order polynomial (up to 6th order) to enable prediction of new branch members. Once branches were found quantum numbers were assigned, using predictions from the *ab initio* constants as a starting guide, and the data fitted to a Watson asymmetric top Hamiltonian in the J' representation.²⁵ A sample spectrum is shown in Fig. 2 to indicate the typical

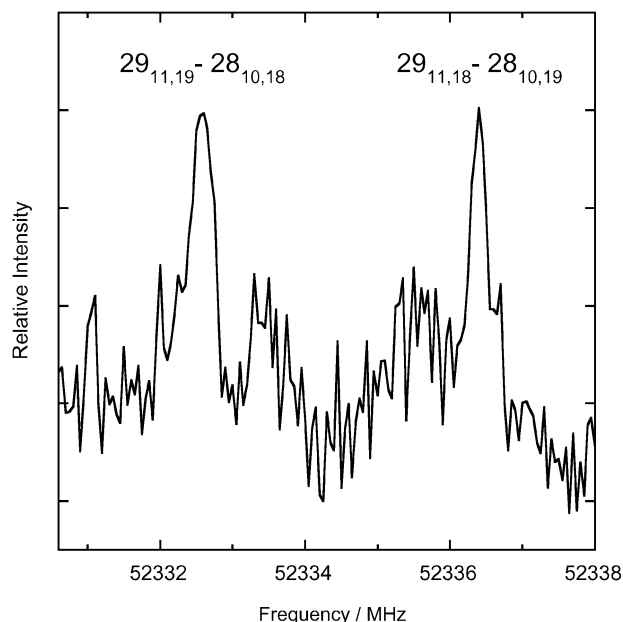


Fig. 2 Sample spectrum of phenanthridine at 52.3 GHz showing the $29_{11,19}-28_{10,18}/29_{11,18}-28_{10,19}$ asymmetry doublet.

Table 2 Experimental transition frequencies and fit residuals *o*–*c* for phenanthridine (MHz)

$J''_{K_a'',K_c''} - J''_{K_a'',K_c''}$	Frequency	<i>o</i> – <i>c</i>
22 _{12,11} –21 _{11,10} /22 _{12,10} –21 _{11,11}	48021.75(3)	0.01
15 _{15,0} –14 _{14,1} /15 _{15,1} –14 _{14,0}	48119.82(3)	–0.02
20 _{13,7} –19 _{12,8} /20 _{13,8} –19 _{12,7}	48392.05(3)	–0.03
30 _{9,21} –29 _{8,22}	48480.86(2)	–0.01
25 _{11,15} –24 _{10,14} /25 _{11,14} –24 _{10,15}	48570.98(3)	–0.03
32 _{9,24} –31 _{8,23}	48595.44(2)	0.02
18 _{14,4} –17 _{13,5} /18 _{14,5} –17 _{13,4}	48747.88(3)	–0.02
28 _{10,19} –27 _{9,18}	48952.29(3)	–0.07
28 _{10,18} –27 _{9,19}	48978.81(3)	0.03
23 _{12,12} –22 _{11,11} /23 _{12,11} –22 _{11,12}	48989.94(4)	–0.01
16 _{15,1} –15 _{14,2} /16 _{15,2} –15 _{14,1}	49098.35(4)	0.01
21 _{13,8} –20 _{12,9} /21 _{13,9} –20 _{12,8}	49366.65(3)	0.01
31 _{9,22} –30 _{8,23}	49513.24(2)	0.03
19 _{14,5} –18 _{13,6} /19 _{14,6} –18 _{13,5}	49725.25(3)	–0.02
29 _{10,19} –28 _{9,20}	49892.92(3)	0.03
24 _{12,13} –23 _{11,12} /24 _{12,12} –23 _{11,13}	49955.68(2)	–0.02
17 _{15,2} –16 _{14,3} /17 _{15,3} –16 _{14,2}	50076.79(6)	0.05
32 _{9,23} –31 _{8,24}	50629.17(2)	0.00
20 _{14,6} –19 _{13,7} /20 _{14,7} –19 _{13,6}	50702.05(3)	–0.02
30 _{10,21} –29 _{9,20}	50710.91(3)	–0.08
30 _{10,20} –29 _{9,21}	50802.27(3)	0.07
18 _{15,3} –17 _{14,4} /18 _{15,4} –17 _{14,3}	51054.93(4)	–0.01
23 _{13,10} –22 _{12,11} /23 _{13,11} –22 _{12,10}	51311.84(3)	0.03
16 _{16,0} –15 _{15,1} /16 _{16,1} –15 _{15,0}	51404.56(4)	–0.04
31 _{10,22} –30 _{9,21}	51547.72(3)	–0.07
31 _{10,21} –30 _{9,22}	51710.12(3)	0.05
26 _{12,15} –25 _{11,14} /26 _{12,14} –25 _{11,15}	51878.32(3)	–0.05
19 _{15,4} –18 _{14,5} /19 _{15,5} –18 _{14,4}	52032.90(3)	0.03
24 _{13,12} –23 _{12,11} /24 _{13,11} –23 _{12,12}	52281.98(2)	0.03
29 _{11,19} –28 _{10,18}	52332.66(3)	–0.06
29 _{11,18} –28 _{10,19}	52336.41(3)	0.07
32 _{10,23} –31 _{9,22}	52341.52(3)	–0.02
17 _{16,1} –16 _{15,2} /17 _{16,2} –16 _{15,1}	52383.11(4)	0.00
32 _{10,22} –31 _{9,23}	52622.32(2)	0.00
22 _{14,8} –21 _{13,9} /22 _{14,9} –21 _{13,8}	52653.37(6)	–0.02
27 _{12,16} –26 _{11,15} /27 _{12,15} –26 _{11,16}	52834.47(4)	0.03
20 _{15,5} –19 _{14,6} /20 _{15,6} –19 _{14,5}	53010.41(3)	–0.01
33 _{10,24} –32 _{9,23}	53075.61(3)	–0.05
25 _{13,13} –24 _{12,12} /25 _{13,12} –24 _{12,13}	53250.13(3)	0.01
18 _{16,2} –17 _{15,3} /18 _{16,3} –17 _{15,2}	53361.51(4)	–0.01
33 _{10,23} –32 _{9,24}	53548.21(3)	–0.02
23 _{14,9} –22 _{13,10} /23 _{14,10} –22 _{13,9}	53627.57(3)	–0.01
34 _{10,25} –33 _{9,24}	53728.16(3)	0.00
21 _{15,6} –20 _{14,7} /21 _{15,7} –20 _{14,6}	53987.48(5)	0.00
26 _{13,14} –25 _{12,13} /26 _{13,13} –25 _{12,14}	54216.00(3)	–0.05
35 _{10,26} –34 _{9,25}	54271.89(3)	0.01
19 _{16,3} –18 _{15,4} /19 _{16,4} –18 _{15,3}	54339.81(4)	0.04
34 _{10,24} –33 _{9,25}	54501.76(3)	–0.01
24 _{14,10} –23 _{13,11} /24 _{14,11} –23 _{13,10}	54600.52(3)	–0.04
17 _{17,0} –16 _{16,1} /17 _{17,1} –16 _{16,0}	54689.31(3)	–0.02
22 _{15,7} –21 _{14,8} /22 _{15,8} –21 _{14,7}	54963.96(3)	0.02
20 _{16,4} –19 _{15,5} /20 _{16,5} –19 _{15,4}	55317.81(4)	0.03
25 _{14,11} –24 _{13,12} /25 _{14,12} –24 _{13,11}	55572.16(3)	0.02
18 _{17,1} –17 _{16,2} /18 _{17,2} –17 _{16,1}	55667.87(4)	0.02
23 _{15,8} –22 _{14,9} /23 _{15,9} –22 _{14,8}	55939.70(3)	0.03
21 _{16,5} –20 _{15,6} /21 _{16,6} –20 _{15,5}	56295.46(3)	–0.01
26 _{14,12} –25 _{13,13} /26 _{14,13} –25 _{13,12}	56542.14(3)	0.02
19 _{17,2} –18 _{16,3} /19 _{17,3} –18 _{16,2}	56646.25(4)	–0.03
24 _{15,9} –23 _{14,10} /24 _{15,10} –23 _{14,9}	56914.53(3)	–0.01
22 _{16,6} –21 _{15,7} /22 _{16,7} –21 _{15,6}	57272.75(4)	0.02
20 _{17,3} –19 _{16,4} /20 _{17,4} –19 _{16,3}	57624.56(5)	0.00
25 _{15,10} –24 _{14,11} /25 _{15,11} –24 _{14,10}	57888.42(6)	0.03
18 _{18,0} –17 _{17,1} /18 _{18,1} –17 _{17,0}	57974.01(5)	–0.04
23 _{16,7} –22 _{15,8} /23 _{16,8} –22 _{15,7}	58249.47(5)	–0.02
21 _{17,4} –20 _{16,5} /21 _{17,5} –20 _{16,4}	58602.68(6)	0.04
26 _{15,11} –25 _{14,12} /26 _{15,12} –25 _{14,11}	58861.04(3)	–0.04
19 _{18,1} –18 _{17,2} /19 _{18,2} –18 _{17,1}	58952.54(3)	–0.02
24 _{16,8} –23 _{15,9} /24 _{16,9} –23 _{15,8}	59225.63(3)	0.01
22 _{17,5} –21 _{16,6} /22 _{17,6} –21 _{16,5}	59580.40(3)	–0.04
20 _{18,2} –19 _{17,3} /20 _{18,3} –19 _{17,2}	59931.00(3)	–0.01

Table 2 (continued)

$J''_{K_a'',K_c''} - J''_{K_a'',K_c''}$	Frequency	<i>o</i> – <i>c</i>
25 _{16,9} –24 _{15,10} /25 _{16,10} –24 _{15,9}	60201.03(2)	0.02
23 _{17,6} –22 _{16,7} /23 _{17,7} –22 _{16,6}	60557.88(4)	0.01
21 _{18,3} –20 _{17,4} /21 _{18,4} –20 _{17,3}	60909.33(4)	0.01
19 _{19,0} –18 _{18,1} /19 _{19,1} –18 _{18,0}	61258.74(4)	0.00
24 _{17,7} –23 _{16,8} /24 _{17,8} –23 _{16,7}	61534.87(3)	0.01
22 _{18,4} –21 _{17,5} /22 _{18,5} –21 _{17,4}	61887.49(4)	0.04
20 _{19,1} –19 _{18,2} /20 _{19,2} –19 _{18,1}	62237.29(4)	0.04
25 _{17,8} –24 _{16,9} /25 _{17,9} –24 _{16,8}	62511.33(3)	0.02
23 _{18,5} –22 _{17,6} /23 _{18,6} –22 _{17,5}	62865.36(4)	0.02
21 _{19,2} –20 _{18,3} /21 _{19,3} –20 _{18,2}	63215.74(3)	0.03
24 _{18,6} –23 _{17,7} /24 _{18,7} –23 _{17,6}	63842.89(4)	–0.02
22 _{19,3} –21 _{18,4} /22 _{19,4} –21 _{18,3}	64194.09(3)	0.04
20 _{20,0} –19 _{19,1} /20 _{20,1} –19 _{19,0}	64543.39(3)	–0.01
23 _{19,4} –22 _{18,5} /23 _{19,5} –22 _{18,4}	65172.22(3)	0.00
21 _{20,1} –20 _{19,2} /21 _{20,2} –20 _{19,1}	65521.93(4)	0.01
33 _{15,9} –32 _{14,18} /33 _{15,18} –32 _{14,19}	65621.25(3)	0.04
31 _{16,15} –30 _{15,16} /31 _{16,16} –30 _{15,15}	66030.40(3)	0.01
22 _{20,2} –21 _{19,3} /22 _{20,3} –21 _{19,2}	66500.43(4)	0.05
27 _{21,6} –26 _{20,7} /27 _{21,7} –26 _{20,6}	73697.57(4)	0.01
25 _{22,3} –24 _{21,4} /25 _{22,4} –24 _{21,3}	74048.05(4)	0.03
30 _{20,10} –29 _{19,11} /30 _{20,11} –29 _{19,10}	74320.16(4)	–0.01
23 _{23,0} –22 _{22,1} /23 _{23,1} –22 _{22,0}	74397.20(5)	–0.01
28 _{21,7} –27 _{20,8} /28 _{21,8} –27 _{20,7}	74675.14(3)	0.00
26 _{22,4} –25 _{21,5} /26 _{22,5} –25 _{21,4}	75026.24(4)	–0.06
31 _{20,11} –30 _{19,12} /31 _{20,12} –30 _{19,11}	75295.80(4)	0.02
24 _{23,1} –23 _{22,2} /24 _{23,2} –23 _{22,1}	75375.73(2)	–0.01
29 _{21,8} –28 _{20,9} /29 _{21,9} –28 _{20,8}	75652.36(4)	–0.04
34 _{19,15} –33 _{18,16} /34 _{19,16} –33 _{18,15}	75902.33(2)	–0.03
27 _{22,5} –26 _{21,6} /27 _{22,6} –26 _{21,5}	76004.44(4)	0.03
32 _{20,12} –31 _{19,13} /32 _{20,13} –31 _{19,12}	76270.72(4)	–0.03
25 _{23,2} –24 _{22,3} /25 _{23,3} –24 _{22,2}	76354.21(3)	0.00
30 _{21,9} –29 _{20,10} /30 _{21,10} –29 _{20,9}	76629.26(5)	–0.01
28 _{22,6} –27 _{21,7} /28 _{22,7} –27 _{21,6}	76982.25(5)	–0.08
26 _{23,3} –25 _{22,4} /26 _{23,4} –25 _{22,3}	77332.64(4)	0.02
24 _{24,0} –23 _{23,1} /24 _{24,1} –23 _{23,0}	77681.73(3)	–0.03
30 _{23,7} –29 _{22,8} /30 _{23,8} –29 _{22,7}	81244.79(3)	0.01
28 _{24,4} –27 _{23,5} /28 _{24,5} –27 _{23,4}	81595.50(4)	0.01
33 _{22,11} –32 _{21,12} /33 _{22,12} –32 _{21,11}	81867.23(3)	–0.02
26 _{25,1} –25 _{24,2} /26 _{25,2} –25 _{24,1}	81944.79(4)	0.00
31 _{23,8} –30 _{22,9} /31 _{23,9} –30 _{22,8}	82222.33(3)	0.06
36 _{21,15} –35 _{20,16} /36 _{21,16} –35 _{20,15}	82478.92(3)	0.02
29 _{24,5} –28 _{23,6} /29 _{24,6} –28 _{23,5}	82573.67(2)	0.00
27 _{25,2} –26 _{24,3} /27 _{25,3} –26 _{24,2}	82923.28(4)	0.01
28 _{25,3} –27 _{24,4} /28 _{25,4} –27 _{24,3}	83901.74(3)	0.05
26 _{26,0} –25 _{25,1} /26 _{26,1} –25 _{25,0}	84250.72(3)	–0.03
27 _{26,1} –26 _{25,2} /27 _{26,2} –26 _{25,1}	85229.24(3)	–0.03

S/N and line shapes obtained. The eventual assignment, listed in Table 2, was arrived at by the ability of the fit to predict new transitions both within V band and in W band (72 to 85 GHz). The final fitted constants are given in Table 3. Despite comparably high *J* and *K* transitions in the data set for such a large rigid molecule, except for Δ_J and Δ_K no other higher order centrifugal distortion constants were needed or determined in the fit. All of the transitions observed are *b*-type connecting rotational levels of comparably low energy (corresponding to $F_J < 36 \text{ cm}^{-1}$) and are accessible to our system because of the cold rotational temperature (*ca.* 10 K) and the sizeable value of μ_b . A search for *a*-type transitions was unsuccessful because strong transitions do not appear in the millimetre wave region accessible to us at the temperature of our jet expansion.

The value of the inertial defect $\Delta_0 = I_c^0 - I_b^0 - I_a^0$ in Table 4 is large and negative, which is indicative of either non planarity or a large contribution from out of plane vibrations. While it appears reasonable to assume planarity for the present kind of

Table 3 Rotational and centrifugal distortion constants of phenanthridine (MHz)

Constant	Value ^a
A	1642.45814(39)
B	557.73024(66)
C	416.51092(75)
$\Delta_J \times 10^6$	3.17(22)
$\Delta_K \times 10^6$	55.34(59)
N_{jines}	116
rms	0.030
wrms ^b	0.94

^a Numbers in brackets are 1σ from the least squares fit. ^b Weighted rms, dimensionless.

Table 4 Inertial defects $\Delta = I_c - I_b - I_a$ ($\text{amu } \text{\AA}^2$) and energetically low-lying out-of-plane modes ($<400 \text{ cm}^{-1}$, obtained at the B3LYP/6-311G** level of theory) of phenanthridine and related molecules

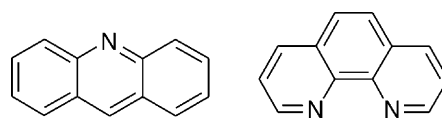
Molecule	Lowest oop modes				Δ
Quinoline ^a	173	182	401	—	-0.1341
Isoquinoline ^b	171	185	386	—	-0.1379
Azulene ^b	180	188	273	—	-0.1510
Carbazole ^c	105	152	271	286	-0.3602
Phenanthridine ^d	96	101	227	245	-0.4688 (44)

^a Inertial defect taken from ref. 5. ^b Inertial defect taken from ref. 32. ^c Inertial defect taken from ref. 8. ^d Inertial defect obtained in the present work.

aromatic system an additional test geometry optimization at the B3LYP/6-311G** level of theory was performed starting with a non planar geometry which converged at the planar structure. Oka²⁶ has thoroughly investigated a number of planar molecules with low out-of-plane vibrations and for aromatic and aliphatic molecules with a single large out-of-plane vibration successfully derived empirical formulae to calculate and explain negative inertial defects as low as $\Delta = -0.8 \text{ amu } \text{\AA}^2$. For molecules with more than just one low out-of-plane mode this is not possible in a straightforward manner, but, qualitatively, by comparing the out-of-plane modes of a range of molecules such as quinoline, azulene and carbazole in Table 4 it can be seen that the trend is to larger negative inertial defects as the number of low frequency out-of-plane modes increases and the magnitude of the vibrational frequency decreases. Some experimental vibrational frequencies and/or vibrational frequency calculations have been reported in the literature (quinoline/isoquinoline, *e.g.* ref. 27; azulene, *e.g.* ref. 28; carbazole, *e.g.* ref. 29) but for the sake of comparability we have performed here calculations at a single level of theory (B3LYP/6-311G**) and provide the results in Table 4. As can be seen from this comparison, the vibrational frequencies in phenanthridine are generally lower than those for (iso)quinoline, azulene and carbazole and a large negative inertial defect is thus expected as a result of these four very low frequency out-of-plane modes.

IV. Conclusions

The gas-phase rotational spectrum of a small PANH, phenanthridine, has been measured for the first time. The resultant

**Fig. 3** Molecular structures of acridine (left) and 1,10-phenanthroline (right).

molecular constants given in Table 3 are of sufficient accuracy to provide useful transition frequencies for a radio astronomical search for this species in space. At arbitrary temperatures of 20 and 100 K, respectively, which span an excitation range commonly found in interstellar and circumstellar media the strongest transitions are *b*-type and peak around 65 and 145 GHz. Predicted uncertainties for those transitions should be better than 1 km s^{-1} in equivalent radial velocity corresponding to a fraction of the linewidth for most astronomical sources with the exception of dark clouds (such as TMC-1), where typical linewidths are of the order of 0.5 km s^{-1} .

Follow-up laboratory investigations of the phenanthridine rotational spectrum require a different spectrometer, such as a molecular beam Fourier transform microwave system [*e.g.* ref. 30, and references therein] capable of measuring *a*-type and low *J* transitions as well as resolving the hyperfine structure (hfs) due to nitrogen quadrupole coupling. Since no hfs was observed in the present study, the nuclear quadrupole coupling constants could not be determined experimentally. However, they were obtained theoretically at the B3LYP/cc-pVTZ level of theory to be $\chi_{aa} = -0.54 \text{ MHz}$, $\chi_{bb} = -2.18 \text{ MHz}$, and $\chi_{cc} = +2.72 \text{ MHz}$.

The success of this study indicates that other PANH species with similar vapour pressures and sizes to phenanthridine, such as the tricyclic molecules acridine, a monoaza derivative of anthracene, and 1,10-phenanthroline, a diaza variant of phenanthrene (see Fig. 3), and probably also tetracyclic systems such as the ones shown in ref. 10 are amenable to be studied by free-jet microwave absorption spectroscopy. Larger PANH molecules, though, have even lower vapour pressures and may require a different experimental approach for vaporization. Additionally, their small rotational constants demand a different spectral region for optimal detection and measurement. Here, a combination of laser ablation and Fourier transform microwave spectroscopy [*e.g.* ref. 31] is expected to be very powerful.

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