

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/256253617>

Microwave spectrum and ^{14}N quadrupole coupling constants of carbazole

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · NOVEMBER 1988

Impact Factor: 1.6 · DOI: 10.1016/0022-2860(88)80278-3

CITATIONS

12

READS

9

4 AUTHORS, INCLUDING:



Francis J. Lovas

National Institute of Standards and Technology

287 PUBLICATIONS 9,068 CITATIONS

SEE PROFILE



G.T. Fraser

National Institute of Standards and Technology

93 PUBLICATIONS 2,380 CITATIONS

SEE PROFILE

MICROWAVE SPECTRUM AND ^{14}N QUADRUPOLE COUPLING CONSTANTS OF CARBAZOLE*

R.D. SUENRAM, F.J. LOVAS and G.T. FRASER

National Bureau of Standards, Gaithersburg, MD 20899 (U.S.A.)

P.S. MARFEY

Department of Biological Sciences, State University of New York, Albany, NY 12222 (U.S.A.)

(Received 1 February 1988)

ABSTRACT

The microwave spectrum of carbazole was observed and analyzed in the 8–14 GHz region using a pulsed molecular-beam Fabry Perot microwave spectrometer. Carbazole was vaporized in a heated nozzle source and was entrained in neon carrier gas before expansion into the Fabry Perot cavity. The rotational transitions were fitted using a rigid rotor Hamiltonian without centrifugal distortion parameters. The rotational constants are $A = 2253.1985(2)$ MHz, $B = 594.1861(2)$ MHz and $C = 470.3503(1)$ MHz. The inertial defect is small ($-0.36 \mu\text{Å}^2$) and consistent with a planar molecule.

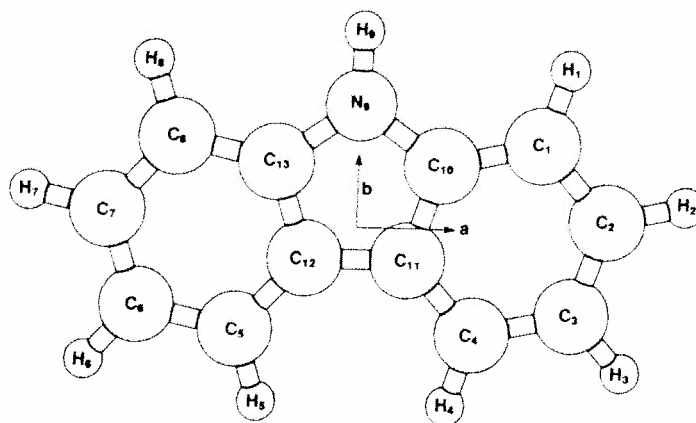
The high resolution available with the instrument (~ 10 kHz) allowed the determination of the ^{14}N nuclear quadrupole coupling constants as $\chi_{aa} = 2.0697(40)$ MHz, $\chi_{bb} = 1.8719(35)$ MHz and $\chi_{cc} = -3.9416(35)$ MHz. A comparison of the electronic environment of the nitrogen atom was made for the series pyrrole, indole and carbazole.

INTRODUCTION

Carbazole (Fig. 1), one of the major coal-tar constituents, is chemically related to pyrrole, indole and carboline. It is also one of the major degradation products of strychnine, an alkaloid found in the seeds of *Strychnos nux-vomica* L. [1]. Carboline derivatives of carbazole are found in overheated protein-containing foods. They are produced by pyrolysis of L-tryptophan, an amino acid residue found in proteins [2,3]. All of these compounds produced by pyrolysis of food proteins are highly mutagenic and carcinogenic.

Previous laser-spectroscopic work on carbazole and carbazole complexes with water and ammonia was performed by Honegger et al. [4]. The crystal and molecular structure of carbazole was solved by Kurahashi et al. [5]. The molecule was found to be approximately planar in the crystal with the two benzene

*Dedicated to the memory of Professor Walter Gordy.



CARBAZOLE

Fig. 1. The carbazole molecule showing the atom numbering and principal axes.

rings of the molecule making an angle of 1.63° . This slightly bent structure might be due to intermolecular interactions in the crystal field. The electron density contour of the hydrogen atom on nitrogen is elongated in the direction normal to the molecular plane. This suggests two possibilities for the hybridization of the nitrogen atom: either sp^2 hybridization with the hydrogen atom located essentially in the plane of the molecule and undergoing out-of-plane oscillations, or sp^3 hybridization with the hydrogen atom located on either side of the molecular plane and undergoing inversion motion as in the case of ammonia. Pure sp^3 hybridization of nitrogen in the crystal was ruled out by the finding that the out-of-plane distance of the hydrogen was only 0.22 \AA instead of 0.6 \AA as would be required for pure sp^3 hybridization. Thus, in the crystal it appears that nitrogen hybridization is closer to sp^2 than sp^3 . This result may explain the so-called N-H and H-4 cross-ring coupling observed in the proton magnetic resonance spectrum of carbazole ($J = 0.7\text{--}0.9 \text{ Hz}$) [6]. The lone pair of electrons on the nitrogen would be expected to participate in forming resonance structures with double bonds between the nitrogen and C₁₀ or C₁₃. These structures would require an sp^2 hybridization of the relevant nitrogen orbitals.

In an effort to gain a better understanding of carbazole in the gas phase we have undertaken a rotational analysis of the molecule using a pulsed-nozzle Fourier-transform microwave spectrometer. In addition, the large size of the carbazole molecule ($\text{C}_{12}\text{H}_9\text{N}$) provides a good test of the sensitivity of the instrument and allows us to assess the feasibility of the instrument for the rotational analysis of other large non-volatile molecular species.

EXPERIMENTAL

Details of the instrument have been presented elsewhere [7] and only a brief description will be given here. The instrument employs a Fabry-Perot micro-

wave cavity and a pulsed-nozzle source. The species of interest is entrained in an inert carrier gas which is expanded through a 0.5 mm diameter hole into the Fabry-Perot cavity. The adiabatic expansion cools the gas to near 1 K. As the molecules enter the center of the cavity, a short microwave pulse ($1-4 \mu\text{s}$) is delivered to the cavity. Several microseconds after the initial microwave excitation, the free-induction decay of the molecules is followed for a period of $\sim 256 \mu\text{s}$. Typically 2000 free-induction decay signals are averaged and then Fourier transformed to generate a spectrum.

One of the major difficulties associated with this experiment is that carbazole is non-volatile and must be heated to $\sim 150-160^\circ\text{C}$ in order to provide a sufficient concentration in the molecular beam for microwave spectroscopy. The heated nozzle [8] has a concentric, moat-like, reservoir for holding the sample and is heated via a small band heater. Usually in these experiments argon is the carrier gas of choice since it provides a cold beam ($\sim 1 \text{ K}$) and is relatively inexpensive. For the work described here, it was found that carbazole transitions were extremely weak in argon. Presumably this is due to the high degree of complex formation ($\text{Ar}_n \cdots \text{carbazole}_m$) in the expansion process. When a mixture of 90% neon/10% helium was employed, the carbazole transitions were 3-4 times more intense than with argon.

A sample spectral trace of the $3_{31}-2_{20}$ rotational transition is shown in Fig. 2. The three peaks arise from the ^{14}N nuclear quadrupole hyperfine splitting of the rotational transition. The spectrum is the average of 2000 free-induction decay signals. The use of neon as an expansion gas leads to additional Doppler

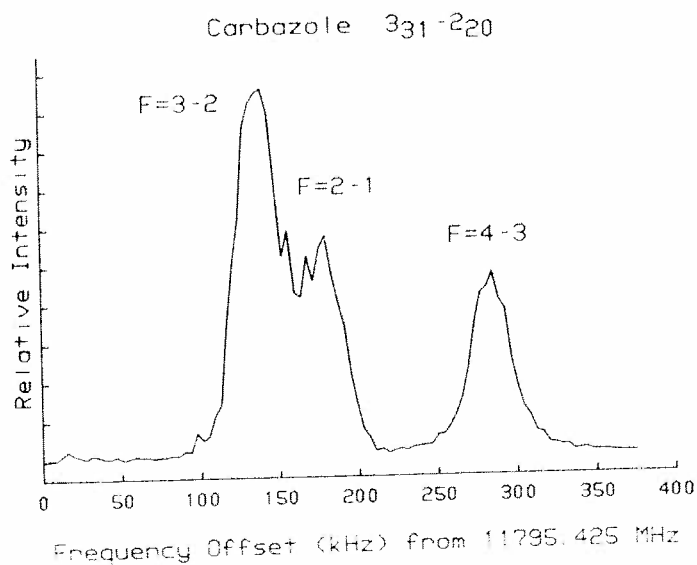


Fig. 2. Spectral scan of the $3_{31}-2_{20}$ rotational transition obtained by averaging a total of 2000 free-induction decay signals.

broadening of the microwave transitions since the velocity of the neon beam is larger (~ 1.4 times) than that of the argon beam. It should be noted that the $F=4-3$ hyperfine component in Fig. 2 has a linewidth of ~ 30 kHz. With argon as a carrier gas the linewidths range from 10 to 20 kHz. The precision of the measurements is typically better than 4 kHz.

SPECTRAL PREDICTIONS AND ROTATIONAL ANALYSIS

The expected symmetry of carbazole in the gas phase is planar C_{2v} leading to a b -type rotational spectrum. Based on our success with indole [9] we were confident in our ability to model the structure with parameters derived from benzene [10] and pyrrole [11]. The structural parameters used are given in Table 1 and the resulting rotational constants are listed in Table 2.

Fourteen rotational transitions in the frequency range ~ 8 –14 GHz were measured (Table 3). These transitions ranged from $J=2-9$ and $K_p=0-4$. The

TABLE 1

Geometric parameters^a used in the prediction of rotational constants of carbazole

<i>Benzene ring</i> ^b	
$r_{CC} = 1.3964$	$\angle CCC = 120$
$r_{CH} = 1.0831$	$\angle CCH = 120$
<i>Pyrrole ring</i> ^c	
$C_{11}-C_{12} = 1.417$	$\angle C_{10}-N-C_{13} = 109.8$
$N-C_{10} = N-C_{13} = 1.3764$	$\angle C_{11}-C_{12}-C_{13} = \angle C_{10}-C_{11}-C_{12} = 107.4$
$H-N = 0.996$	$\angle C_{11}-C_{10}-N = \angle C_{12}-C_{13}-N = 107.7$
$C_{10}-C_{11} = C_{12}-C_{13} = 1.3964$	

^aBond lengths in ångströms, angles in degrees. ^bRef. 10. ^cRef. 11.

TABLE 2

Predicted and observed rotational constants (MHz) and observed ^{14}N quadrupole coupling constants (MHz) of carbazole

	Predicted values ^a	Observed values	Obs. - Calc.
A	2290	2253.1985 (2) ^b	-39
B	597	594.1861 (2)	-3
C	473	470.3503 (1)	-4
J^c	0	$-0.3602 (4) \mu\text{Å}^2$	
χ_{aa}		2.0697 (40)	
χ_{bb}		1.8719 (35)	
χ_{cc}		$-3.9416 (35)$	

^aFrom the parameters in Table 1. ^bThe numbers in parentheses represent one standard deviation of the fit. ^c $J \equiv I_c - I_b - I_a$.

TABLE 3
Measured transition frequencies for carbazole

Transition $J'_{K'_{\perp}K'_{\parallel}} - J''_{K''_{\perp}K''_{\parallel}}$	$F' - F''$	Frequency ^a (MHz)	Obs. - Calc. (kHz)
$3_{2,2}-2_{1,1}$		8170.649(1) ^b	3
	2-1	8170.179	-2.0
	4-3	8170.518	2.7
	3-2	8171.117	0.0
$3_{2,1}-2_{1,2}$		8575.410(2)	1
	3-2	8574.298	0.4
	4-3	8575.735	1.1
	2-1	8576.498	1.0
$4_{2,3}-3_{1,2}$		9048.526(2)	3
	3-2	9048.113	0.9
	5-4	9048.340	0.9
	4-3	9049.067	0.1
$9_{1,9}-8_{0,8}$		9308.165(5)	-4
	9-8	9308.380	-3.0
$5_{2,4}-4_{1,3}$		9864.612(2)	5
	4-3	9864.209	-1.5
	6-5	9864.393	0.9
	5-4	9865.194	-2.9
$4_{2,2}-3_{1,3}$		9890.189(4)	-3
	4-3	9889.052	-1.1
	5-4	9890.567	-0.8
	3-2	9891.098	0.8
$3_{3,1}-2_{2,0}$		11795.650(2)	0
	3-2	11795.560	3.6
	2-1	11795.609	-2.1
	4-3	11795.709	-0.7
$3_{3,0}-2_{2,1}$		11802.556(2)	4
	3-2	11802.409	-1.0
	2-1	11802.570	0.7
	4-3	11802.628	-1.3
$8_{4,4}-8_{3,5}$		11905.866(4)	0
	8-8	11905.818	-1.6
$4_{4,0}-4_{3,1}$		12033.367(3)	-4
	4-4	12032.856	1.1
	5-5	12033.552	-1.2
	3-3	12033.731	-1.8
$4_{4,1}-4_{3,2}$		12034.939(3)	-1
	4-4	12034.419	-2.5
	5-5	12035.128	0.8
	3-3	12035.308	-0.7
$4_{3,1}-3_{2,2}$		12881.141(2)	0
	4-3	12880.915	-1.8
	5-4	12881.220	-2.5
	3-2	12881.360	4.8
$5_{3,2}-4_{2,3}$		13976.251(3)	-1
	5-4	13976.014	-0.3
	6-5	13976.338	0.5
	4-3	13976.410	-9.2

^aThe estimated uncertainty in the actual measurements of the hyperfine components is ≤ 4 kHz.

^bThese are the hypothetical unsplit center frequencies of the transitions. The number in parentheses is twice the standard deviation of the rigid rotor fit for that transition.

TABLE 4

Comparison of the bonding characteristics associated with the NH group

	Pyrrole	Indole	Carbazole
eQq_{\parallel} (MHz)	1.45	1.644	1.872
eQq_{\perp} (MHz)	1.21	1.735	2.070
i_{σ} (NH)	0.22	0.24	0.27
π_c	0.48	0.38	0.29
c^-	0.24	0.36	0.48

transitions (including hyperfine components) were fitted in an iterative fashion to a rigid rotor Hamiltonian [12]. No distortion constants were required in the fit. The resulting rotational constants are given in Table 2.

The hyperfine analysis employed 35 hyperfine components. The results of this analysis are shown in Table 4 where a comparison is made between pyrrole, indole and carbazole.

DISCUSSION

Although a detailed structural investigation is beyond the scope of this paper, a number of interesting points can be discussed. In a previous publication we presented an analysis relating the ^{14}N quadrupole coupling constants in indole to the electronic environment around the nitrogen atom [9]. A comparison was made with the analogous molecule, pyrrole, using the equations and assumptions given by Gordy and Cook [13]. We now extend this analysis to the next larger member of the series, carbazole, using the same methods.

The parameters given in Table 4 are defined as follows: eQq_{\parallel} and eQq_{\perp} are the components of the ^{14}N quadrupole tensor parallel to and perpendicular to (in the molecular plane) the N-H bond (for carbazole $eQq_{\parallel} = eQq_{bb}$ and $eQq_{\perp} = eQq_{aa}$), i_{σ} (NH) is the ionic character of the N-H bond, π_c is the amount of the π bonding by the electrons in the p_z orbital of the nitrogen atom (orbital perpendicular to the molecular plane) and c^- is the negative charge on the nitrogen atom, in electron units.

The comparisons in Table 4 indicate that the ionic character in the N-H bond (i_{σ} (NH)) increases slightly as one goes from pyrrole to carbazole. The π bonding of the p_z electrons shows a marked decrease as more "benzene" rings are attached to pyrrole. Correspondingly, as one might expect, the negative charge on the nitrogen atom (c^-) increases. Together these results show that in the series pyrrole to carbazole the hybridization at the nitrogen atom changes from sp^2 to sp^3 character. This suggests that the molecular framework around the nitrogen would prefer to be non-planar but the bonding constraints of the two benzene rings prevent this from occurring.

In general, one can enumerate a number of classical resonance structures for carbazole. Of these structures, there are two which have a classical double bond from the nitrogen to C₁₀ or C₁₃. Both forms also have a C₁₁-C₁₂ double bond. The information derived from the ¹⁴N nuclear quadrupole evidence suggests that these two resonance forms become less important in describing the bonding in carbazole. It also indicates that there is little delocalization of electrons from one benzene ring to the next and that the local electronic structures of the benzene rings resemble that of free benzene. This may account for the good agreement between observed and calculated rotational constants, since the calculated structure employs benzene structural parameters to derive the rotational constants. These results also suggest that in the gas phase carbazole would exhibit less of the N-H and H-4 cross-ring coupling as is observed in the solution NMR experiments [6].

The overall geometry of the molecule is planar or very nearly so. The small negative inertial defect of $\Delta = -0.3602 \mu\text{\AA}^2$ could indicate a slight non-planarity in the molecule or it could arise from one or more low frequency out-of-plane bending vibrations. It should be noted that c-type transitions were searched for, but not observed.

One of the more interesting aspects of the study is how well the experimental and calculated rotational constants agree. This same good agreement was also observed in the indole study [9] and it implies that the structures of derivatives of indole and carbazole can be modeled fairly closely (at least with respect to the ring geometry) by using structural parameters from benzene and pyrrole. This is useful because of the difficulty in obtaining high resolution spectra for such large ring molecules.

REFERENCES

- 1 R.B. Woodward, M.P. Cava, W.D. Ollis, A. Hunger, H.U. Daeniker and K. Schenker, *J. Am. Chem. Soc.*, 76 (1954) 4749.
- 2 H. Akimoto, A. Kawai, H. Nomura, M. Nagao, T. Kawachi and T. Sugimura, *Chem. Lett.*, 9 (1977) 1061.
- 3 K. Wakabayashi, K. Tsuji, T. Kosuge, K. Takeda, K. Yamaguchi, K. Shudo, Y. Iitaka, T. Okamoto, T. Yahagi, M. Nagao and T. Sugimura, *Proc. Jpn. Acad.*, 54 (B) (1978) 569.
- 4 E. Honegger, R. Bombach and S. Leutwyler, *J. Chem. Phys.*, 85 (1986) 1234.
- 5 M. Kurahashi, M. Fukuyo and A. Shimada, *Bull. Chem. Soc. Jpn.*, 42 (1969) 2174.
- 6 P.J. Black and M.L. Heffernan, *Aust. J. Chem.*, 18 (1965) 353.
- 7 F.J. Lovas and R.D. Suenram, *J. Chem. Phys.*, 87 (1987) 2010.
- 8 F.J. Lovas, R.D. Suenram, G.T. Fraser, C.W. Gillies and J. Zozom, *J. Chem. Phys.*, 88 (1987) 722.
- 9 R.D. Suenram, F.J. Lovas and G.T. Fraser, *J. Mol. Spectrosc.*, 127 (1988) 472.
- 10 A. Cabana, J. Bachand and J. Giguere, *Can. J. Phys.*, 52 (1974) 1949.
- 11 L. Nygaard, J.T. Nielson, J. Kirchheiner, G. Maltesen, J.R. Andersen and G.O. Sorensen, *J. Mol. Struct.*, 3 (1969) 491.
- 12 W.H. Kirchhoff and D.R. Johnson, *J. Mol. Spectrosc.*, 45 (1973) 159.
- 13 W. Gordy and R.L. Cook, *Microwave Molecular Spectra*, Interscience, New York, 1970, pp. 601-605.

