

## LETTER TO THE EDITOR

The Prediction of the Rotational Constants of Polyacetylene Compounds  $H-(C\equiv C)_n-C\equiv N$ 

Recently microwave emission lines of interstellar polyacetylene compounds cyanobutadiyne  $H-(C\equiv C)_2-C\equiv N$  (1, 2) and cyanohexatriyne  $H-(C\equiv C)_3-C\equiv N$  (3) have been discovered based on the laboratory microwave studies of these compounds by Kroto and his collaborators (4, 5). In extending this series to even higher polyacetylene compounds, an attempt was made to estimate the rotational constants by calculation because of the difficulty of the chemical preparation of these compounds in the laboratory. The result of such a calculation has led to the recent successful detection of the two rotational transitions  $J = 25 \rightarrow 24$  and  $J = 18 \rightarrow 17$  of cyano-octatetrayne  $H-(C\equiv C)_4-C\equiv N$  in Heiles' Cloud 2 (6). The difference between the predicted value of  $B_0 = 290.5233$  MHz and the observed value of 290.5184 MHz was 5.1 kHz corresponding to an accuracy of prediction of  $1.7 \times 10^{-5}$ . I believe there is some ground to claim that this agreement, albeit surprising, is not fortuitous. In view of the possible future use of this method of calculation for radioastronomy and molecular spectroscopy and of the puzzling nature of the result, I describe it explicitly in this letter.

Rotational constants of molecules are normally calculated from the estimated molecular structure (7). However, the accuracy of the frequency prediction needed for a radio astronomical search makes this approach futile because in addition to the difficulty of obtaining accurate structure, the vibration-rotation correction due to zero-point vibration is not easily calculable. Rather we used a straightforward numerical extrapolation using the series of rotational constants available for  $H-(C\equiv C)_n-C\equiv N$  with  $n = 0, 1, 2$ , and 3.

First we calculate moments of inertia  $I_n^c(\mathbf{r})$  for  $n = 0, 1, 2$ , and 3 using an assumed set of structural parameters

$$\mathbf{r} = [r(C-H), r(C\equiv C), r(C-C), r(C\equiv N)]. \quad (1)$$

The same values are assumed for all like bonds without taking into account the subtleties such as the dependence of a bond length on the neighboring bonds (8) and the Morino-Bastiansen shrinkage (9).  $I_n^c(\mathbf{r})$  is then subtracted from the observed effective moments of inertia  $I_n^0 = h/8\pi^2 B_n^0$ , and the residuals are fit to the polynomial,

$$\sigma_n = I_n^0 - I_n^c(\mathbf{r}) = a_0 + a_1 n + a_2 n^2 + a_3 n^3. \quad (2)$$

With a proper, but by no means special, choice of the structural parameters  $\mathbf{r}$ , it was seen that the coefficients of the polynomial converge to zero rapidly. The effective moment of inertia  $I_n^0$  of  $H-(C\equiv C)_n-C\equiv N$  can then be calculated from

$$I_n^0 = I_n^c(\mathbf{r}) + \sigma_n. \quad (3)$$

Several examples of the calculation are given in Table I. No careful choice of the assumed parameters was made except that they yield  $\sigma_n$  that show a definite trend to either positive or negative values as  $n$  increases from 0 to 3. Contrary to the initial expectation, it was found that this calculation gives consistent values of  $B_0$  for a wide range of structural parameters in spite of the fact that the "correction"  $\sigma_n$  varies wildly. This consistency gave some confidence that indeed the correct value was obtained. It is interesting to note that, in order for the coefficients of the polynomial in Eq. (2) to converge and thus to obtain a good  $B_0$  value, the residues  $\sigma_n$  have to be sizeable, that is, we have to use structural parameters

TABLE I  
Examples of Calculated  $B_0$  for  $\text{H}-(\text{C}\equiv\text{C})_n-\text{C}\equiv\text{N}$

No.	Assumed parameters ( $\text{\AA}$ )				$\sigma_n$ ( $\text{amu}\text{\AA}^2$ )	$B_0$ (MHz)
	C-H	C $\equiv$ C	C-C	C $\equiv$ N		
1	1.057	1.22	1.3485	1.16	8.519	290.5236
2	1.05	1.22	1.35	1.16	6.661	290.5236
3	1.06	1.21	1.36	1.16	5.846	290.5229
4	1.062	1.215	1.357	1.157	4.023	290.5235
5	1.05	1.22	1.36	1.159	-6.233	290.5223
6	1.06	1.22	1.365	1.158	-12.771	290.5239

which are not too close to the real values. For example if we use a set of parameters such as [ $r(\text{CH}) = 1.0569$ ,  $r(\text{C}\equiv\text{C}) = 1.2223$ ,  $r(\text{C}-\text{C}) = 1.3550$ , and  $r(\text{C}\equiv\text{N}) = 1.1606$ ] (4), we obtain a poorly predicted value because the values of  $\sigma_n$  are too small and vary in sign thus requiring a higher-order polynomial for their fit.

The method given above can be easily extended to general cases and to two-dimensional extrapolation by using more than one series of compounds.

After this simple calculation and the successful application of it to the detection of interstellar  $\text{H}-(\text{C}\equiv\text{C})_n-\text{C}\equiv\text{N}$  (6), we are left with the following two questions.

- (1) Is the agreement still fortuitous? The calculated values may be converging to a value which is off from the real value. After all, the difference of 5.1 kHz between the observed and predicted values is five times the fluctuation of predicted values. It is tempting to say no to this question and that this method is applicable also to the other cases. If we use it for the after-the-fact prediction of  $B_0$  for  $\text{H}-(\text{C}\equiv\text{C})_3-\text{C}\equiv\text{N}$  by using a polynomial of second order, we obtain a value with an accuracy of  $3 \times 10^{-4}$ , which although less accurate than that for  $n = 4$ , still would have been sufficiently accurate for a radio astronomical search. Since the accuracy of prediction improves with the increasing value of  $n$ , it is likely that  $B_0$  values of  $\text{H}-(\text{C}\equiv\text{C})_n-\text{C}\equiv\text{N}$  with  $n \geq 5$  obtained by this method are meaningful although at some point molecules must become so flexible that the method will start to fail. The rotational constant of  $\text{H}-(\text{C}\equiv\text{C})_5-\text{C}\equiv\text{N}$  is predicted to be 169.0629 MHz.<sup>1</sup> Future observation of this molecule will answer this question.
- (2) If the agreement is not fortuitous, then how do molecules know to behave so well? Adding one link of  $-\text{C}\equiv\text{C}-$  to a polyacetylene chain is a drastic operation; even between  $n = 3$  and  $n = 4$ , it almost doubles the moment of inertia. It is intriguing how the result of such an operation can be predicted so accurately by a simple extrapolation.

#### ACKNOWLEDGMENTS

I would like to thank L. W. Avery, N. W. Broten, and J. M. MacLeod for discussions leading to this work and to L. W. Avery, N. W. Broten, A. E. Douglas, G. Herzberg, J. W. C. Johns, and J. M. MacLeod for their critical reading of this paper.

#### REFERENCES

1. L. W. AVERY, N. W. BROTEN, J. M. MACLEOD, T. OKA, AND H. W. KROTO, *Astrophys. J. Lett.* **209** L173-L175 (1976).
2. N. W. BROTEN, J. M. MACLEOD, T. OKA, L. W. AVERY, J. W. BROOKS, R. X. MCGEE, AND L. M. NEWTON, *Astrophys. J. Lett.* **209** L143-L147 (1976).

<sup>1</sup> This value was calculated by using the structural set 3 in Table I which gives  $a_0 = -0.044892$ ,  $a_1 = 0.713957$ ,  $a_2 = 0.323289$ ,  $a_3 = -0.037806$ , and  $a_4 = 0.001218$  (all in a.m.u.  $\text{\AA}^2$ ). Rotational constants for  $n > 5$  can be calculated using these numbers.

3. H. W. KROTO, C. KIRBY, D. R. M. WALTON, L. W. AVERY, N. W. BROTEN, J. M. MACLEOD, AND T. OKA, *Astrophys. J. Lett.* **219**, L133-L137 (1978).
4. A. J. ALEXANDER, H. W. KROTO, AND D. R. M. WALTON, *J. Mol. Spectrosc.* **62**, 175-180 (1976).
5. C. KIRBY, H. W. KROTO, AND D. R. M. WALTON, to be published.
6. N. W. BROTEN, T. OKA, L. W. AVERY, J. M. MACLEOD, AND H. W. KROTO, *Astrophys. J. Lett.* (1978), to be published.
7. S. WILSON AND S. GREEN, *Astrophys. J. Lett.* **212**, L87-L90 (1977).
8. G. HERZBERG AND B. P. STOICHEFF, *Nature* **175**, 79-81 (1955).
9. Y. MORINO, J. NAKAMURA, AND P. W. MOORE, *J. Chem. Phys.* **36**, 1050-1056 (1962).

TAKESHI OKA

*Herzberg Institute of Astrophysics  
National Research Council of Canada  
Ottawa, Ontario, Canada K1A/OR6*

*Received: January 31, 1978*