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Molecular Structure of Gaseous Cyanogen Azide and Azodicarbonitrile

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The molecules were studied by the gas electron diffraction method. Root mean-square amplitudes of vibration, and correction terms to transfer the electron diffraction parameters R_a to thermal average parameters R_α, were computed from available spectroscopic data. The molecules are *trans* planar about the central N=N bonds. The N≡C–N arrangements deviate slightly from linearity with the N≡C bonds *trans* to the N=N bonds. The following R_α parameters (distances in Å, angles in degrees) and standard deviations corrected for systematic errors were obtained for cyanogen azide: $R(N{\equiv}C) = 1.155(2)$, $R(C-N) = 1.355(2)$, $R(N=N) = 1.261(2)$, $R(\overset{+}{N}=\bar{N}) = 1.121(2)$, $\theta(N{\equiv}C=N) = 175.3(1.4)$, $\theta(C-N=N) = 114.5(0.2)$, and $\theta(N=\overset{+}{N}=\bar{N}) = 169.2(1.6)$, and for azodicarbonitrile (C_{2h}-symmetry): $R(N{\equiv}C) = 1.151(1)$, $R(C-N) = 1.363(2)$, $R(N=N) = 1.261(2)$, $\theta(N{\equiv}C-N) = 172.5(0.3)$, and $\theta(C-N=N) = 113.0(0.2)$. Like in chlorine azide the azide group of cyanogen azide is non-linear. This deviation from linearity as well as the non-linearity of the N≡C–N arrangement were confirmed by *ab initio* calculations.

The infrared and Raman spectra of cyanogen azide and its condensation product, azodicarbonitrile, have previously been recorded and assigned (Refs. 1 and 2). With access to these interesting compounds, an electron diffraction investigation of the molecules seemed worth-while. The results are given in the present paper.

EXPERIMENTAL

Diffraction photographs from samples synthesized in Copenhagen [1,2] were obtained on the Oslo apparatus.[3] The unstable cyanogen azide was transported solved in dimethyl phthalate and distilled into the apparatus from this solution. The nozzle temperatures were about 20°C and the accelerating voltage was about 36 kV. Five plates for each of the two camera distances of about 48 and 20 cm were used for the structure investigation of cyanogen azide. For azodicarbonitrile, six plates from each of the two distances were applied. The plates were photometered in the usual way.[4]

CALCULATION OF u- AND K-VALUES FROM THE NORMAL FREQUENCIES OF THE MOLECULES

To the approximation of small vibrations, the electron diffraction parameter R_a may be related to the equilibrium distance R_e by [5]

$$R_a = R_e + \langle \Delta z \rangle - u^2/R + K + \delta R + \ldots, \quad (1)$$

where

$$K = (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2R, \quad (2)$$

u is the root mean-square amplitude of vibration, $u = (\langle \Delta z^2 \rangle)^{\frac{1}{2}}$, and δR is a small correction for centrifugal distortion. Omitting this term, the effects of harmonic vibrations may be removed by defining the distance parameter R_α according to:[5]

$$R_e + \langle \Delta z \rangle = R_a + u^2/R - K \equiv R_\alpha \quad (3)$$

Then the R_α distances should, except for anharmonic effects, be consistent with the molecular symmetry and geometry.

Due to the closely spaced bonded distances in the molecules it was desirable to know the root-mean square amplitudes of vibration from the spectroscopic data. When the small deviations from linearity of the N≡C−N arrangements appeared during the electron diffraction investigation, knowledge of the K-values for the molecules were of interest to correct the R_a- to R_α-distances in order to compute angles based on R_α models.

Initial calculations by Cyvin [6] indicated that the second assignment for the normal frequencies of cyanogen azide [1] was correct, but that some normal frequencies for azodicarbonitrile [2] had to be reassigned to obtain reasonable force constants. Since the assignment of Ref. 2 was not final, a possible alternative is suggested (Table 2). The calculations were continued on this foundation using a modified [7] computer program by Gwinn.[8] By this program Urey-Bradley force fields were fitted to the normal frequencies by a trial and error procedure.

The normal frequencies are compared to the computed ones in Table 1 and Table 2. The force constants are given in Table 3, the computed u- and

Table 1. Observed and computed normal frequencies for cyanogen azide in cm^{-1}.

	Observed [1]	Computed
ν_1	2248	2261
ν_2	2198	2201
ν_3	1246	1226
ν_4	921	933
ν_5	666	627
ν_6	444	467
ν_7	167	167
ν_8	520	520
ν_9	444	442

Table 2. Observed and computed normal frequencies for azodicarbonitrile in cm^{-1}.

		Observed [2,6]	Computed
ν_1		2176	2188
ν_2		1422	1422
ν_3	A_g	1002	1005
ν_4		482 [a,b]	508
ν_5		282	302
ν_6	B_g	504 [a,b]	508
ν_7		2204	2191
ν_8	B_u	982	981
ν_9		596	585
ν_{10}		152 [a,b]	150
ν_{11}	A_u	574	577
ν_{12}		133	133

[a] Reassignment based on $\nu_9 = 596$; $2\nu_{10} + \nu_9 = 904$, $\nu_{10} = 152$; $\nu_4 - \nu_5 = 200$, $\nu_4 = 482$; $\nu_6 - 2\nu_{10} = 200$, $\nu_6 = 504$. [b] Not directly observed.

Table 3. Force constants for cyanogen azide and azodicarbonitrile.

	Cyanogen azide	Azodicarbonitrile
K(1,2) [a]	16.1	16.1
K(2,3) [a]	5.5	5.5
K(3,4) [a]	8.5	7.4
K(4,5) [a]	17.8	
F(2,4) [a]	1.2	0.46
H(1,2,3) [b]	0.53	0.49
H(2,3,4) [b]	0.35	0.57
H(3,4,5) [b]	0.44	
θ(1,2,3,4) [c]	0.53	0.56
θ(2,3,4,5) [c]	0.44	0.13

[a] Stretching force constants in mdyn $Å^{-1}$. [b] Bending force constants in mdyn Å rad^{-2}. [c] Out-of-plane bending force constants in mdyn Å rad^{-2}.

Table 4. u- and K-values for cyanogen azide and azodicarbonitrile in Å.

	Cyanogen azide			Azodicarbonitrile		
Distance	K [a]	u^a	u^b	K^a	u^a	u^b
1–2	0.0065	0.0352		0.0115	0.0352	
2–3	0.0034	0.0446		0.0064	0.0447	
3–4	0.0037	0.0397		0.0020	0.0416	
4–5	0.0077	0.0336				
1–3	0.0028	0.0485	0.0475(25)	0.0106	0.0490	0.0502(10)
1–4	0.0017	0.0793	0.0758(15) [c]	0.0078	0.0819	0.0803(19)
1–5	0.0003	0.1121	0.1141(41)	0.0023	0.0732	0.0754(15)
3–5	0.0033	0.0462	0.0454(26)			
2–4	0.0023	0.0609	0.0558(24)	0.0038	0.0671	0.0568(12)
2–5	0.0017	0.0757	0.0758(15) [c]	0.0016	0.0672	0.0718(46)
1–6				0.0003	0.0757	0.0823(26)

[a] Computed for the force fields of Table 3. [b] Experimental values. [c] Average value of $u(1-4)$ and $u(2-5)$.

K-values are listed in Table 4, and the numbering of the atoms are illustrated in Fig. 1.

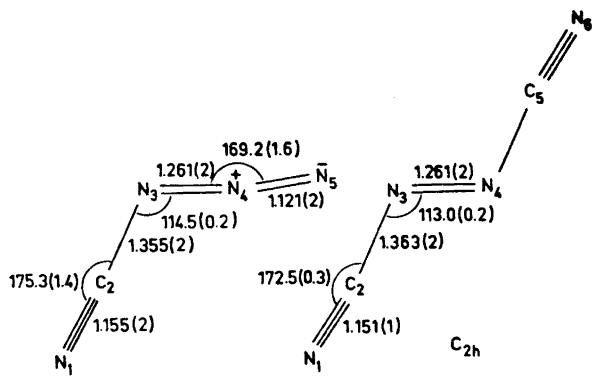

Fig. 1. Numbering of the atoms of cyanogen azide and azodicarbonitrile. Corrected R_α parameters (distances in Å and angles in degrees) and standard deviations from Table 6 are given.

THE STRUCTURE INVESTIGATION

The electron diffraction data were processed and analyzed in the usual way.[4] Partial waves scattering factors computed for 35 kV electrons [9] based upon analytical HF potentials for the atoms [10] were applied. The first backgrounds were drawn on the levelled intensity curves, and the molecular intensities obtained were modified by $s/|f_N'||f_C'|$.

The backgrounds were adjusted on the individual intensities from each plate by comparing intensities calculated for the first models of the molecules to the experimental intensities. The curves were then scaled and averaged, and the average correlation coefficients [11] and the standard deviations at each point of the intensities were computed. The correlation in the data were as usual for the Oslo apparatus, and in the final least-squares refinements p_2 and p_3 of the weight matrix [11] were -0.6 and 0.11 for the 48 cm data and -0.6 and 0.115 for the data from the 20 cm camera distance. The constants w_1, s_1, w_2, and s_2 for the diagonal part of the weight matrix [4] were for both of the molecules 4.5, 5.5, 0.06, and 10.0, and 4.5, 11.0, 0.008, and 20.0 for the 48 cm and 20 cm data, respectively. The two curves were kept separated in the final refinements and they were given the same weight. The molecular intensities are illustrated in Fig. 2.

For data and theory without systematic errors, about two thirds of the differences between the experimental and calculated intensities should be within the standard deviations of the average intensities, and only 1 per cent of the differences should be greater than 2.5 times the standard deviations. This seems to be the case for the middle part of the 20 cm camera distance data, while the differences for the middle part of the 48 cm data seem larger than indicated by the standard deviations. The large differences at small

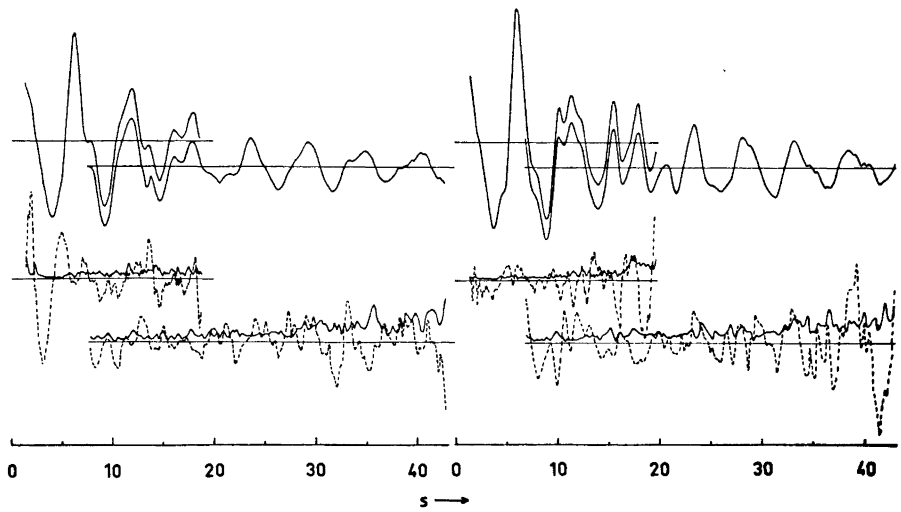

Fig. 2. Average experimental molecular intensities, standard deviations of the average intensities and differences between experimental and calculated molecular intensities (broken curves) for cyanogen azide (left) and azodicarbonitrile (right). The standard deviations and differences were multiplied by a factor of 10.

s-values of the 48 cm data for cyanogen azide could not be included in a smooth background. Corresponding differences for azodicarbonitrile were removed by an unsmooth background. The constants for the diagonal

Table 5. Distances R_a in Å and angles for cyanogen azide and azodicarbonitrile from least-squares refinements.

	Cyanogen azide		Azodicarbonitrile		
	A	B	B	C	A
$R(1,2)$	1.1569(15)	1.1591(17)	1.1605(5)	1.1604(6)	1.1585(5)
$R(2,3)$	1.3531(12)	1.3550(12)	1.3662(6)	1.3658(8)	1.3629(6)
$R(3,4)$	1.2608(12)	1.2620(11)	1.2599(12)	1.2601(12)	1.2581(12)
$R(4,5)$	1.1272(16)	1.1265(18)			
$\theta(1,2,3)$	178.23(1.09)	175.32(1.39)	172.54(0.35)		173.65(0.33)
$\theta(2,3,4)$	114.56(0.20)	114.48(0.21)	113.04(0.13)		112.96(0.14)
$\theta(3,4,5)$	167.78(1.35)	169.24(1.56)			
$R(1,3)$	2.5097(17)	2.5065(16)	2.5157(7)	2.5155(9)	2.5175(7)
$R(1,4)$	3.2557(77)	3.2689(92)	3.2735(14)	3.2702(20)	3.2687(14)
$R(1,5)$	4.2545(43)	4.2541(44)	4.5490(10)	4.5515(17)	4.5533(11)
$R(3,5)$	2.3745(18)	2.3713(17)			
$R(2,4)$	2.1995(21)	2.1982(21)	2.1883(10)	2.1876(11)	2.1857(10)
$R(2,5)$	3.2730(80)	3.2562(98)	3.4181(13)	3.4167(45)	3.4186(13)
$R(1,6)$			5.6853(15)	5.6877(32)	5.6975(15)
$\mathbf{V'PV} \times 10^{-3}$	2.88	2.95	3.57	3.49	3.99

A. The R_a distances were consistent with the molecular geometries.
B. The corresponding R_α distances were consistent with the molecular geometries.
C. All the distances were independent parameters.

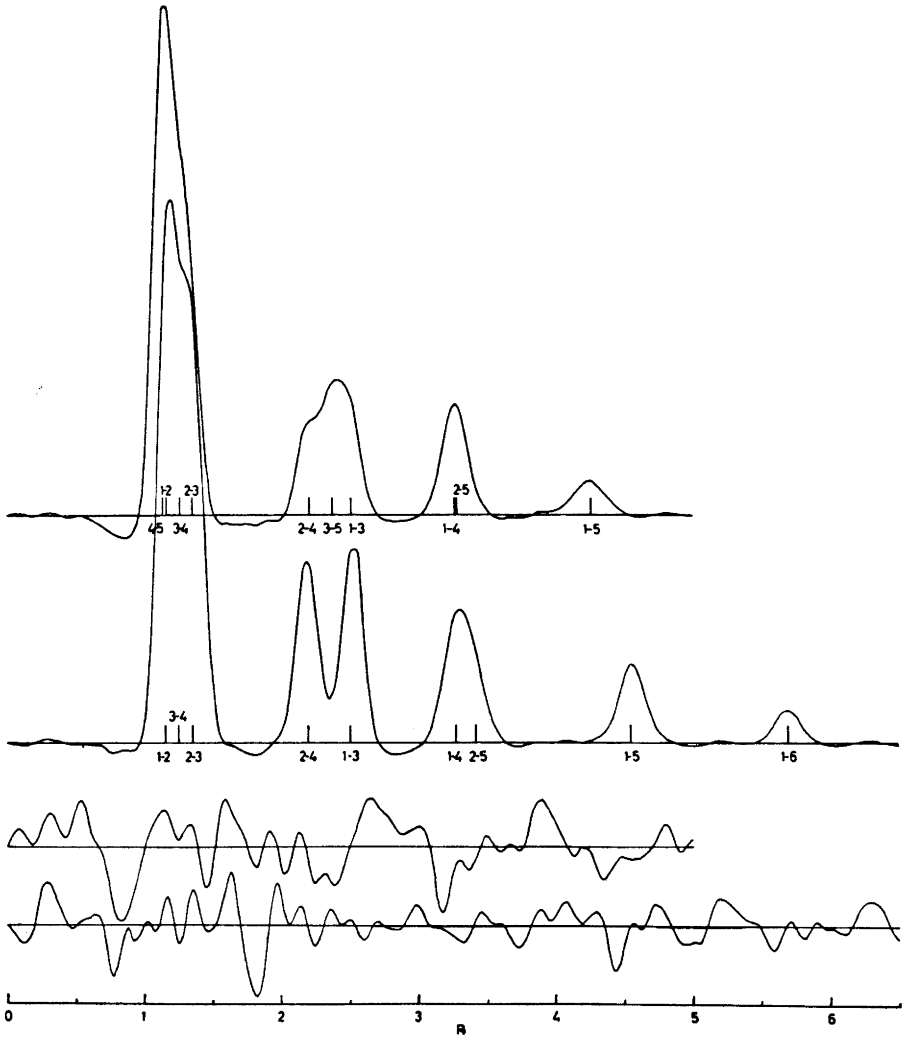

Fig. 3. Experimental radial distribution functions for cyanogen azide (top) and azodicarbonitrile, and differences between experimental and calculated functions. The differences were multiplied by a factor of 10. For the experimental functions, calculated intensities were added inside $s = 5$ Å^{-1}, and the intensities were multiplied by a damping function of exp $(-0.0018\ s^2)$ before the functions were computed.

part of the weighting matrix give for both molecules very little weight to the data inside $s = 5$ Å^{-1}, and calculated values were added to the experimental intensities inside $s = 5$ Å^{-1} before computing the radial distribution functions.

The results of different least-squares refinements are given in Table 5. Attempts to determine the u-values of all the bonded distances gave unreasonable results, and these u-values were fixed on the calculated values (Table 4). In cyanogen azide $R(1,3)$ is so close to $R(2,5)$ that reasonable u-values were not obtained independently for the two distances. These u-values were therefore started on equal values and given the same shifts in the least squares refinements. By this procedure an average value is determined. The other u-values could be obtained by least-squares calculations, and their values are included in Table 4.

The data for the two camera distances were connected applying the scale factors of the least-squares refinements and adding theoretical intensities for the inner unobserved parts. Radial distribution functions were computed from these intensities and compared to functions computed from the models of Table 5 B with u-values from Table 4, using the experimental ones whenever possible. These curves are illustrated in Fig. 3.

Distances from data of the Oslo apparatus seem presently low by about 0.1 % in comparison to an R_a(C–C) in benzene of 1.397 Å,[12] but the magnitude of this correction is uncertain. In Table 6, 0.1 % has been added to the R_α distances corresponding to the R_a distances of Table 5, B, and the standard deviations have been corrected for systematic uncertainties in the distances of 0.1 %.

Table 6. Corrected R_α distances (Å) and angles for cyanogen azide and azodicarbonitrile.

	Cyanogen azide	Azodicarbonitrile
$R(N\equiv C)$	1.155(2)	1.151(1)
$R(C-N)$	1.355(2)	1.363(2)
$R(N=N)$	1.261(2)	1.261(2)
$R(\overset{+}{N}=\overset{-}{N})$	1.121(2)	
$\theta(N\equiv C-N)$	175.3(1.4)	172.5(0.3)
$\theta(C-N=N)$	114.5(0.2)	113.0(0.2)
$\theta(N=\overset{+}{N}=\overset{-}{N})$	169.2(1.6)	

Ab initio calculations. Table 7 reports results of *ab initio* calculations of the energy of 3 configurations of cyanogen azide, consistent with the electron diffraction results. The basis set of Ref. 13 was applied.

DISCUSSION

The molecules have *trans* configurations about the central N=N bonds. The amount of any *cis* configurations present cannot be more than a few per cent. Refinements started with the N≡C bonds *cis* to the central N=N bonds converge to *trans* positions of the former bonds for both molecules. This deviation from linearity of the N≡C–N arrangement is significant for

Table 7. Results of *ab initio* calculations of the energy (in a.u.) of 3 configurations, A, B and C, of cyanogen azide. Distances in Å, angles in degrees.

	A [a]	B [b]	C [c]
Distances			
1 – 2	1.158	1.158	1.158
2 – 3	1.354	1.354	1.354
3 – 4	1.260	1.260	1.260
4 – 5	1.127	1.127	1.127
Angles			
1,2,3	180.0	180.0	178.0
2,3,4	114.4	114.4	114.4
3,4,5	180.0	168.0	168.0
Energy	−255.12984	−255.13146	−255.13176
Sum of atomic energies			−255.012

[a] Straight N≡C−N and azide groups. [b] Straight N≡C−N and bent azide groups. [c] Bent N≡C−N and azide groups.

azodicarbonitrile. For cyanogen azide the significance of the deviation may be somewhat doubtful if the effect were based on the electron diffraction result for only this molecule.

Some of the K-values necessary to transfer the R_a- to the R_α-distances are relatively large, especially in the case of azodicarbonitrile. For this molecule, distances from the refinement constrained by an R_α model agree favourably with the independently determined distances (Table 5, B, C), and the agreement is better than from the refinement constrained by an R_a model not corrected for shrinkage (Table 5, B, A). For cyanogen azide, where the number of geometric parameters are greater and the number of atoms are fewer than in azodicarbonitrile, the R_a model fits the data slightly better than the R_α model (Table 5, A, B). All the distances could not be determined independently for this molecule.

The u-values computed from the force fields agree favourably with the obtainable experimental ones (Table 4). Only the values of distance 2 – 4 of azodicarbonitrile disagree significantly in terms of the uncorrected least-squares standard deviations. The computed u-values of the non-bonded distances are more uncertain than for the bonded ones, and the least-squares standard deviations may be too small. The uncertainties of the force constants are probably large. Other sets of values might reproduce the normal frequencies just as well and give reasonable u- and K-values.

The conclusion of the electron diffraction investigation is that the molecules are *trans* planar about the central N=N bonds with small deviations from linearity of the N≡C−N arrangements with the N≡C bonds *trans* to the N=N bonds. The best estimates of the structure parameters and their standard deviations are given in Table 6.

Comparing the parameters of Table 6, the N=N distances are the same in the two molecules. The variations in R(N≡C), R(C–N) and θ(C–N=N) are consistent with a somewhat greater contribution from the linear structure $::\overset{-1}{\ddot{N}}=C=\overset{+1}{N}=\overset{+1}{N}=\overset{-1}{\ddot{N}}::$ in cyanogen azide than from $::\overset{-1}{\ddot{N}}=C=\overset{+1}{N}=\overset{+1}{N}=C=\overset{-1}{\ddot{N}}::$ in azodicarbonitrile. If R_a parameters are compared, the R(C≡N)'s do not fit into this scheme. The nonlinearity of the N≡C–N̈ arrangements could be due to the lone pair at the nitrogen atoms. The larger deviation from linearity of azodicarbonitrile as compared to cyanogen azide may be explained by an attraction of the lone pair by the formal +1 charge at N_4 in the latter molecule, thereby increasing the effect on θ(N=N=N) and decreasing the effect on θ(N≡C–N).

Ab initio calculations have been carried out for azodicarbonitrile.[13] In agreement with the present result, the possible *cis* conformer is computed to be unstable by about 20 kcal mol^{-1} in relation to the *trans* form.

The central N=N bonds may be compared to the values of 1.25 Å in azomethane [14,15] and chlorine azide.[16] For azide [17] and methyl azide [18] values of 1.24 Å are given. The terminal N=N bond of cyanogen azide should be compared to the values of 1.13 Å in chlorine azide,[16] azide,[17] and methyl azide.[18] Deviation from linearity of the –N=N=N arrangement is reported for chlorine azide [16] with 8° towards the *trans* position.

Nonlinear C–C≡N arrangements are known. For tetracyanoethylene oxide [19] the effect is explained by delocalization of the oxygen lone pair into antibonding π orbitals of the cyano group. The deviation is about 4° or about half the size of the N̈–C≡N deviation in azodicarbonitrile where the lone pair is situated at the atom next to the cyano group. Due to the charge distribution in cyanogen azide,[20] a lone pair delocalization to the cyano group might be less than in azodicarbonitrile.

Whereas to the best of our knowledge no other structure determination of azodicarbonitrile has been carried out, microwave investigators [20,21] have studied cyanogen azide. In Ref. 21 a structure was derived, building on 2

Table 8. Comparison of the structure of cyanogen azide as formed by microwave technique (MW) and by electron diffraction (ED). Distances in Å, angles in degrees.

	MW	ED
Distances		
1–2	1.164(5)	1.155(2)
2–3	1.312(20)	1.355(2)
3–4	1.252(10)	1.261(2)
4–5	1.133(10)	1.121(2)
Angles		
1,2,3	176.0(2.0)	175.3(1.4)
2,3,4	120.2(1.0)	114.5(0.2)
3,4,5	180 (assumed)	169.2(1.6)

Table 9. Microwave rotational constants A, B, and C, of cyanogen azide from Ref. 21 compared to rotational constants (in MHz) from the electron diffraction model of Table 6.

	MW	ED
A	38066.8 ± 0.15	38108.7
B	3185.15 ± 0.025	3185.8
C	2933.30 ± 0.025	2940.0

isotopic substitutions ($^{15}N{\equiv}C-N_3$ and $N{\equiv}^{13}C-N_3$) and an assumed linear azide group. By necessity this structure is in disagreement with ours (Table 8). In Table 9 the rotational constants corresponding to the ED model of Table 8 are confronted with the experimental ones.[20,21] The agreement is quite satisfactory.

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