

# On the Molecular Structure of Gaseous Cyanogen Isocyanate, $\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$

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The title compound recently produced by Hocking and Gerry by pyrolysis of silver cyanate has been found among the many products of pyrolysis ( $\text{S}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{OCS}$ ,  $\text{N}_2\text{S}_2$ (?)) of  $\text{O}=\text{C}-\text{N}=\text{S}=\text{N}-\text{S}$  (I), 5-oxo-1,3-2,4-dithiadiazole, and identified by its microwave spectrum. By pyrolysis of a mixture of  $^{15}\text{N}$ -enriched species of I microwave spectra of  $\text{N}\equiv\text{C}-^{15}\text{N}=\text{C}=\text{O}$  and  $^{15}\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$  were obtained. The molecular model of cyanogen isocyanate presented by Hocking and Gerry may consequently be slightly modified.

Our current studies of pyrolysis of 5-membered ring compounds<sup>1-4</sup> include  $\text{O}=\text{C}-\text{N}=\text{S}=\text{N}-\text{S}$ , or 5-oxo-1,3-2,4-dithiadiazole (I). At 1000 °C and  $p=30-40$  mTorr a product of pyrolysis P was obtained, its microwave spectrum (m.w.s.) observed and assigned. P was identified as cyanogen isocyanate,  $\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$  (Fig. 1) which has been produced recently by Hocking and Gerry by pyrolysis of  $\text{AgOCN}$  and characterized by its m.w.s.<sup>5</sup> Its experimental rotational constants  $B$  and  $C$  are included in Table 1. By pyrolysis of I a multitude of products is obtained besides P. To sort out nitrogen-containing species an available

mixture of I (49 %),  $\text{O}=\text{C}-^{15}\text{N}=\text{S}=\text{N}-\text{S}$  (21 %),  $\text{O}=\text{C}-\text{N}=\text{S}=\text{N}-^{15}\text{N}-\text{S}$  (21 %) and  $\text{O}=\text{C}-^{15}\text{N}=\text{S}=\text{N}-^{15}\text{N}-\text{S}$  (9 %) was pyrolyzed. As expected it yielded P and two  $^{15}\text{N}$ -monosubstituted species S (with a small isotope effect) and L (with a large) in sufficient quantities. The m.w.s. of P, L and S were in almost correct intensity ratios, all three displaying nitrogen quadrupole coupling fine structure. The instability of I (*vide infra*) and the small available quantity (40 mg) of moderately  $^{15}\text{N}$ -enriched sample prevented the time-consuming recording of resolved quadrupole coupling patterns of S and L (neither was it resolved for P in Ref. 5). Thus, the resulting rotational constants are less accurate than usual. Nevertheless, the inclusion of  $B$  and  $C$  for S and L in a discussion of a molecular model for the isotopic 'family' P, S and L appears to be of some interest. All values of  $B$  and  $C$  for S and L were derived using the distortion constants and inertial defect of Ref. 5, agreeing fully with our own observations on P.

## EXPERIMENTAL

$\text{O}=\text{C}-\text{N}=\text{S}=\text{N}-\text{S}$  (I) prepared and analyzed earlier<sup>6</sup> was obtained by us by a method easily amenable to  $^{15}\text{N}$  enrichment.<sup>7</sup> Freshly prepared I kept *in vacuo* at 0 °C in an available volume of 30 ml developed a pressure of 10 mTorr in 1 min, rising to 15 mTorr in the following 5 min. The corresponding data at 20 °C are 45 and 60 mTorr. Samples were kept at -20 °C or lower and distilled *in vacuo* at 0 °C into a liquid air trap prior to use. In pyrolysis experiments vapors of P or of the  $^{15}\text{N}$ -enriched sample were pumped through a 10 cm hot section (1000 °C) of quartz tubing continuing through a 10 cm cold (20 °C)

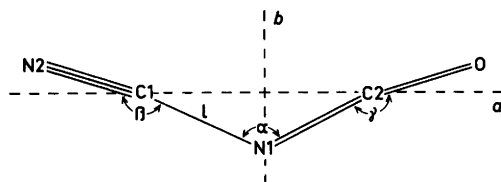


Fig. 1. Numbering of atoms in planar  $\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$  as placed in its principal axes ( $a, b$ ) system.

Table 1. Experimental (Exp.) and model (Mod.) rotational constants (MHz) of  $\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$ ,  $\text{N}\equiv\text{C}-^{15}\text{N}=\text{C}=\text{O}$  and  $^{15}\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$ .

	B	Exp.-Mod.	C	Exp.-Mod.
<b>Species</b>				
$\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$				
Experimental	2699.03 <sup>5</sup>		2597.86 <sup>5</sup>	
<b>Models</b>				
Hocking and Gerry <sup>5</sup>	2698.44	0.47	2604.02	-6.16
<i>ab initio</i> <sup>8,a</sup>	2743.55	-44.52	2596.18	1.68
This paper model 1	2699.36	-0.33	2597.39	0.47
This paper model 2	2699.12	-0.09	2598.19	-0.33
$\text{N}\equiv\text{C}-^{15}\text{N}=\text{C}=\text{O}$				
Experimental	2699.11 <sup>b</sup>		2594.00 <sup>b</sup>	
<b>Models</b>				
Hocking and Gerry <sup>5</sup>	2698.41	0.60	2600.50	-5.50
<i>ab initio</i> <sup>8,a</sup>	2743.55	-44.44	2590.13	3.87
This paper model 1	2699.34	-0.23	2593.61	0.39
This paper model 2	2699.12	-0.01	2593.80	0.20
$^{15}\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$				
Experimental	2622.41 <sup>b</sup>		2526.52 <sup>b</sup>	
<b>Models</b>				
Hocking and Gerry <sup>5</sup>	2622.94	-0.53	2532.37	-5.85
<i>ab initio</i> <sup>8,a</sup>	2666.73	-44.32	2525.53	0.99
This paper model 1	2623.76	-1.35	2525.97	0.55
This paper model 2	2622.68	-0.27	2526.17	0.35

<sup>a</sup> Planar model. Basis set minimal STO-3G. <sup>b</sup> This paper.

Table 2. Comparison of molecular models of  $\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$ . Atom numbering in Fig. 1. Bond lengths in Å, angles in degrees.

	<i>ab initio</i> <sup>8</sup>	H. and G. <sup>5</sup>	This paper Model 1	Model 2
<b>Distances</b>				
N2=C1	1.160	1.164	1.164	1.164
C1-N1	1.384	1.283 <sup>a</sup>	1.303 <sup>a</sup>	1.345 <sup>a</sup>
N1=C2	1.256	1.218	1.218	1.218
C2=O	1.176	1.165	1.165	1.165
<b>Angles</b>				
N2-C1-N1	176.1	180	180	172
C1-N1-C2	123.1	140 <sup>a</sup>	138.47 <sup>a</sup>	129.0 <sup>a</sup>
N1-C2-O	168.7	180	180	169

<sup>a</sup> Derived from experimental data.

section of the same tube in order to finally passing a conventional Stark modulated m.w. spectrometer, cell length 3 m. A suitable production of P, S and L was obtained by keeping I at 20 °C, corresponding

to entrance/exit pressures at the spectrometer of 30/20 mTorr. Experimental rotational transition frequencies of S (13  $\mu_a$ -transitions) and of L (7  $\mu_a$ -transitions), reporting the highest peaks in more

or less resolved quadrupole coupling patterns (triplets) are available on request. Observation of transitions such as  $6_{34} \rightarrow 7_{35}$  at 37114.5 MHz (S) and at 36106.0 MHz (L) at very low fields (10–20 V/cm) proved of great diagnostic value. Comparing the richness of lines observed in Ref. 5 to our spectra of P, S and L it must be realized that pyrolysis of  $\text{AgOCN}^5$  is superior to pyrolysis of I to obtain cyanogen isocyanate.

## DISCUSSION

$\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{O}$  has 7 geometric parameters. Choosing five of these from related molecules<sup>5</sup> an estimate of  $l=1.283$  Å and  $\alpha=140^\circ$  (Fig. 1) was obtained.<sup>5</sup> An estimate of  $l$  building on the hybridization status of C1 and N1 and ignoring shortening due to electron delocalization<sup>9</sup> indicates  $l=1.37$  Å or 0.09 Å longer than in the model of Ref. 5, but much closer to the *ab initio* model.<sup>8</sup> By inclusion of the  $^{15}\text{N}$ -data of this paper  $l=1.303$  Å and  $\alpha=138.47^\circ$  are obtained (Table 2, model 1). Model 2 was obtained taking  $\beta=172^\circ$ <sup>11</sup> and  $\gamma=169^\circ$  (as for angle  $\text{N}=\overset{+}{\text{N}}=\bar{\text{N}}$ , Ref. 11) and adjusting  $l$  and  $\alpha$  to  $l=1.345$  Å and  $\alpha=129^\circ$ . This would mean a considerable approach to the *ab initio* model (Table 2). Qualitatively, *ab initio* estimates of angles like  $\beta$  and  $\gamma$  (Fig. 1) have proved useful,<sup>1,10,11</sup> even to predict a slight twist of a  $\text{CH}_2$  group.<sup>12</sup>

*Acknowledgements.* This investigation has in part been supported by the Danish Natural Sciences Research Council. We are grateful to Dr. G. O. Sørensen of this laboratory for permission to use his program ROTFIT.

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*Acta Chem. Scand. A* 33 (1979) No. 8

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Received March 28, 1979.