

STRUCTURAL STUDIES OF 1,3-DI(*N,N*-DIMETHYLFORMAMIDYL)-2-CYANO GUANIDINE. THE CASE OF A STRONGLY LEWIS BASIC NITROGEN ATOM IN THE CYANO GROUP VIII. CRYSTALLOGRAPHIC STUDIES OF INTRA- AND INTER-MOLECULAR INTERACTIONS

TADEUSZ MAREK KRYGOWSKI* AND ROMANA ANULEWICZ
Department of Chemistry, Warsaw University, ul. Pasteura 1, 02-093 Warsaw, Poland

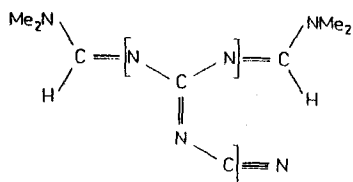
EWA D. RACZYŃSKA
Institute of General Chemistry, Agricultural University, 02-528 Warsaw, Poland

AND

CHRISTIAN LAURENCE
Laboratoire de Spectrochimie Moleculaire, Faculté des Sciences et des Techniques, Université de Nantes, 44 072 Cedex 03, Nantes, France

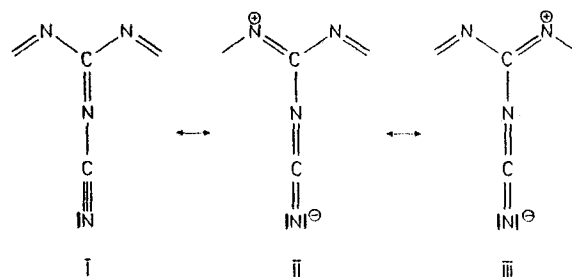
INTRODUCTION

1,3-Di(*N,N*-dimethylformamidyl)-2-cyanoguanidine (CG) contains a cyano group linked directly to the imino nitrogen atom of a guanidine skeleton. The Huheey electronegativity for CN [$\chi(\text{CN}) = 3.84^1$], the substituent inductive constant [$\sigma_1(\text{CN}) = 0.57^2$] and the substituent resonance constant [$\sigma_R^-(\text{CN}) = 1.02^2$] show that cyano is among the most strongly electron-accepting groups in organic chemistry.



In amidines, the site of hydrogen bonding is the imino nitrogen atom.^{3,4} However, the cyano group in CG decreases the hydrogen bond basicity of the imine nitrogen atom as a result of inductive and resonance withdrawing effects (canonical forms I-III) and may change the site of fixation.

The aim of this work was to study how far these effects really operate in CG molecules.



EXPERIMENTAL

IR measurements. IR spectra were recorded on a Bruker IFS 45 WHR Fourier transform spectrometer (Université de Nantes) with 1 cm^{-1} resolution and 256 scans, using KBr cells of 0.1 and 1 mm, and concentrations of solutions of CG of about 5×10^{-3} – 5×10^{-2} M. Solvents were spectroscopic-grade compounds dried over 4 Å molecular sieves before use. The overlapping infrared bands for CG were decomposed using a Bruker curve-fitting software.

Synthesis and x-ray measurements. CG was synthesized by heating (at ca 70 °C) an equimolar mixture of dicyandiamide and dimethylformamide dimethylacetal for about 1 h. The product obtained was recrystallized

from methanol. Unit cell parameters were obtained from the least-squares refinement of 25 reflections in the range $4 \geq 2\theta \geq 25^\circ$. Intensities were collected on a Siemens P3 diffractometer using Mo K α radiation monochromatized by graphite up to a 2θ angle of 50° . An $\omega - 2\theta$ scan was performed ($h \leq 8$, $k \leq 19$, $-13 \leq l \leq 13$); 1721 reflections were collected, 1474 were unique ($R_{\text{int}} = 0.0095$) and 1168 were classified as observed on the basis of the criterion $F \geq 3\sigma(F)$. The data were corrected for Lorentz and polarization effects but no absorption correction was applied.

The structure was solved by direct methods, block-matrix least-squares refinement minimizing $\Sigma w (|F_o| - |F_c|)^2$, weights $w = 1/[\sigma^2(F_o) + 0.001F^2]$. Heavy atoms were refined anisotropically; all H atoms were obtained from a difference map and refined with an isotropic temperature factor, with 127 parameters. Final $R = 0.0591$, $wR = 0.0659$ for 1168 reflections, the final difference Fourier map showed $\Delta\rho_{\text{max}} 0.19$ and $\Delta\rho_{\text{min}} -0.24 \text{ e } \text{\AA}^{-3}$, maximum Δ/σ in final cycle = 0.3, average $\Delta/\sigma = 0.001$.

The computer programs applied were SHELXS⁵ and SHELX-76.⁶ Molecular illustrations were drawn using the PLUTO⁷ package. Atomic scattering factors were taken from Ref. 8.

RESULTS AND DISCUSSION

Crystal data for CG are given in Table 1, atomic positions in Table 2 and bond lengths and bond angles in Table 3. A view of the molecule with the atom numbering scheme is presented in Fig. 1.

The geometry of CG clearly shows localized double bonds C(8)–N(3) and C(3)–N(1), 1.301(4) and 1.308(4) Å long, respectively. Thus, only the part of the π -electron system shown in brackets in the initial formula of CG is taken into account. Application of the HOSE model⁹ to the geometry of this part of the CG molecule results in I = 31.2% and II = 34.4% and

Table 1. Crystal data

Molecular formula	C ₈ N ₆ H ₁₄
Molecular weight	194.24
Space group	$P2_1/n$
Cell dimensions (Å)	$a = 6.289(2)$ $b = 15.788(3)$ $c = 10.847(3)$ $\beta = 101.37(2)^\circ$ $V = 1055.87$
Cell volume (Å ³)	
Molecular multiplicity	$Z = 4$
Calculated density (g cm ⁻³)	1.222
Radiation, λ (Mo K α) (Å)	0.71069
Linear absorption coefficient (cm ⁻¹)	$\mu = 0.8$
Reflections $F > 3\sigma(F)$	1168
R	0.0591
wR	0.0659

Table 2. Atomic fractional coordinates ($\times 10^4$) (ESDs in parentheses) and equivalent isotropic thermal parameters calculated from anisotropic thermal parameters: $B_{\text{eq}} = 8\pi^2 D_u^{1/3} / (\sin \alpha^* \sin \beta^* \sin \gamma^*)^2$, where D_u is the determinant of the U_{ij} matrix

Atom	X/A	Y/B	Z/C	$B_{\text{eq}}(\text{\AA})$
C(1)	3999(4)	50(2)	3080(2)	3.9
N(1)	1940(4)	-49(1)	2414(2)	4.2
C(3)	819(5)	636(2)	2053(2)	4.1
N(2)	-1145(4)	583(1)	1359(2)	4.3
C(5)	-2400(5)	1339(2)	899(3)	5.4
C(6)	-2134(5)	-227(2)	985(3)	5.1
N(3)	4822(4)	839(1)	3374(2)	4.3
C(8)	6780(5)	881(2)	4041(2)	4.5
N(4)	7790(4)	1601(1)	4362(2)	4.8
C(10)	9993(6)	1620(2)	5110(3)	6.5
C(11)	6746(5)	2414(2)	4033(3)	6.0
N(5)	5200(4)	-638(1)	3407(2)	4.6
C(13)	4355(5)	-1390(2)	3033(2)	4.8
N(6)	3841(5)	-2073(2)	2761(3)	6.5

Table 3. Bond lengths (Å) (ESDs in parentheses) and bond angles ($^\circ$) (ESDs in parentheses)

Bond lengths	
N(1)–C(1)	1.362(3)
N(3)–C(1)	1.362(3)
N(5)–C(1)	1.331(3)
C(3)–N(1)	1.308(4)
N(2)–C(3)	1.316(4)
C(5)–N(2)	1.463(4)
C(6)–N(2)	1.445(4)
C(8)–N(3)	1.301(4)
N(4)–C(8)	1.315(4)
C(10)–N(4)	1.461(4)
C(11)–N(4)	1.454(4)
C(13)–N(5)	1.331(4)
N(6)–C(13)	1.147(4)
Bond angles	
C(1)–N(1)–C(3)	117.6(2)
N(1)–C(1)–N(3)	120.4(2)
N(1)–C(1)–N(5)	118.6(2)
C(1)–N(3)–C(8)	116.8(2)
N(3)–C(1)–N(5)	121.0(2)
C(1)–N(5)–C(13)	118.4(2)
N(1)–C(3)–N(2)	120.5(2)
C(3)–N(2)–C(5)	121.7(2)
C(3)–N(2)–C(6)	121.4(2)
C(5)–N(2)–C(6)	116.9(2)
N(3)–C(8)–N(4)	123.1(3)
C(8)–N(4)–C(10)	121.4(2)
C(8)–N(4)–C(11)	121.8(2)
C(10)–N(4)–C(11)	116.8(2)
N(5)–C(13)–N(6)	172.7(3)

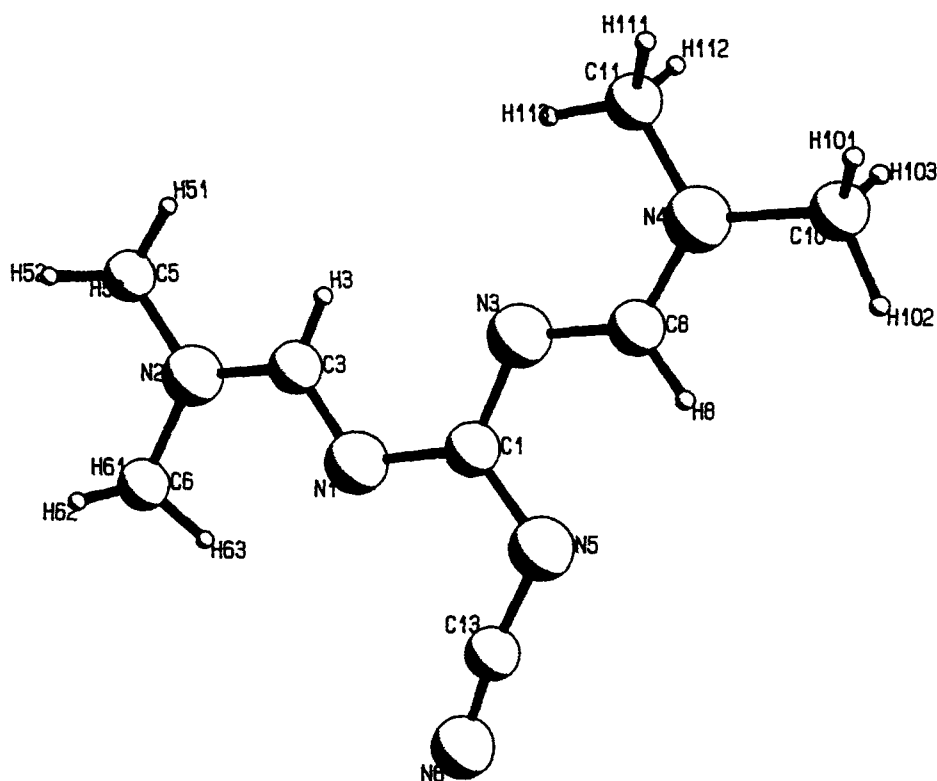


Figure 1. A view of the molecule with the numbering of the atoms

III = 34.4%. Considering unit positive and negative charges in structures III and IV and the weights of these structures, the negative charge at the cyano group nitrogen is -0.688 , whereas at both nitrogen atoms in the amidine skeleton it is $+0.344$. This implies an increase in the basic character of the nitrogen in the cyano group, a decrease in the basic character of both nitrogen atoms in the guanidine skeleton, and a decrease in $\nu(\text{C}\equiv\text{N})$ as shown by the infrared group frequencies.

This last effect is shown in Table 4. A significant decrease in $\nu(\text{C}\equiv\text{N})$ is observed for CG in comparison with acetonitrile as the reference molecule. Moreover, the effect of conjugation is greater in CG than in other conjugated nitriles.

The decrease in the basic character of the imino nitrogen atoms of the guanidine skeleton is illustrated by the fixation of hydrogen-bond donors, such as methanol and *p*-fluorophenol, on the $\text{C}\equiv\text{N}$ group. This is shown by an increase in the frequency of the

Table 4. Effect of conjugation [$\text{D}\cdots\text{C}\equiv\text{N}\leftrightarrow\text{}^+\text{D}\cdots\text{C}=\text{N}:\text{}^-$] on location of IR band $\nu(\text{C}\equiv\text{N})$ in a few selected compounds, CH_3CN , $(\text{CH}_3)_2\text{NCN}$, $(\text{CH}_3)_2\text{NCH}=\text{NCN}$ and $[(\text{CH}_3)_2\text{NCH}=\text{N}]_2\text{C}=\text{NCN}$, in different solvents

Solvent	$\nu(\text{C}\equiv\text{N})$				$\Delta\nu(\text{C}\equiv\text{N}) = \nu(\text{C}\equiv\text{N})_{\text{D}\cdots\text{CN}} - \nu(\text{C}\equiv\text{N})_{\text{MeCN}}$			
	MeCN (1)	Me_2NCN (2)	$\text{Me}_2\text{NCH}=\text{NCN}$ (3)	$(\text{Me}_2\text{NCH}=\text{N})_2\text{C}=\text{NCN}$ (4)	1	2	3	4
CCl_4	2256	2221	2201 ^a	— ^b	0	-35	-55	— ^b
PhCl	2254	2217	2197	2175	0	-34	-57	-79
THF	2252	2218	2197	2176	0	-34	-55	-76
CH_2Cl_2	2255	2217	2197	2172	0	-38	-58	-83

^a Ref. 10.

^b Unmeasurable because of low solubility.

Table 5. Values of $\Delta\nu(\text{OH}) = \nu(\text{OH})^{\text{MeOH}} - \nu(\text{OH})^{\text{MeOH}\cdots\text{B}}$ and $\log K_{\text{HB}}$ for $(\text{CH}_3)_2\text{NCN}$, $(\text{CH}_3)_2\text{NCNH}=\text{CN}$ and $\{(\text{CH}_3)_2\text{NCH}=\text{N}\}_2\text{C}=\text{NCN}$ in CCl_4

Compound	$\Delta\nu(\text{OH})$	$\log K_{\text{HB}}$
$(\text{CH}_3)_2\text{NCN}$	$117.5 \pm 2^{\text{a}}$	$1.56 \pm 0.05^{\text{a}}$
$(\text{CH}_3)_2\text{NCH}=\text{CN}$	$150 \pm 2^{\text{a}}$	$2.09 \pm 0.05^{\text{a}}$
$\{(\text{CH}_3)_2\text{NCH}=\text{N}\}_2\text{C}=\text{NCN}$	$175 \pm 1 - 0^{\text{b}}$	$2.10 \pm 0.20^{\text{c}}$

^a Ref. 10.

^b Because of the poor solubility of CG in CCl_4 , the measurements were carried out in CH_2Cl_2 and an estimated CCl_4 value was calculated from the $\Delta\nu(\text{OH})^{\text{CCl}_4}/\Delta\nu(\text{OH})^{\text{CH}_2\text{Cl}_2}$ correlation.¹¹

^c This work. The measurements were carried out in PhCl and the $\log K_{\text{HB}}$ value in CCl_4 was estimated from a linear free energy relationship between $\log K_{\text{HB}}^{\text{CCl}_4}$ and $\log K_{\text{HB}}^{\text{PhCl}}$.¹¹

$\nu(\text{C}\equiv\text{N})$ band in the hydrogen-bonded complex $p\text{-FC}_6\text{H}_4\text{OH}\cdots\text{CG}$ in comparison with the CG molecule. Additionally, the 175 cm^{-1} shift of the $\nu(\text{OH})$ vibrator of MeOH on hydrogen-bond formation is characteristic of $\text{C}\equiv\text{N}\cdots\text{HO}$ and not of $\text{C}=\text{N}\cdots\text{HO}$ complexation. Table 5 shows that this shift is greater with CG than with other conjugated nitriles. The same is true of the equilibrium constant K_{HB} for hydrogen-bond formation between p -fluorophenol and CG. The stronger the intramolecular charge transfer from the electron-donating atoms attached to the amine skeleton of CG to the accepting nitrogen in the cyano group, the higher are the hydrogen-bonding basicity properties ($\Delta\nu\text{OH}$ and $\log K_{\text{HB}}$) to be expected. The data in Table 5 are in line with this interpretation.

In conclusion, it should be pointed out that owing to very strong conjugative interactions in the CG molecule, hydrogen-bonding sites common for amidine at the imine nitrogen^{3,4} are changed to the nitrogen atom in the cyano group, in full agreement with the structural

data (geometry) of the molecule translated by the HOSE model⁹ into relative weights of canonical structures.

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