

Does Diisooxocyan (OCN–NCO) Exist?

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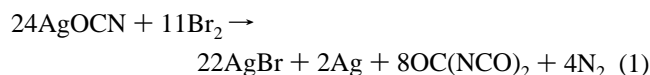
Introduction

The linear cyanate ion $[\text{NCO}]^-$ can be regarded as a pseudohalide ion, and covalently bound species are known which contain the NCO unit coordinated either via oxygen (H–OCN, cyanic acid)¹ or via nitrogen (H–NCO, isocyanic acid).^{1a,c,2} However, most of the known NCO compounds exist in the *iso* form (R–N=C=O, R = halogen, alkyl, aryl).³ (N.B. There are also many trimeric organic OCN derivatives, e.g. triazines and cyanuric acid.³) The structurally related fulminate ion $[\text{CNO}]^-$ is also known (AgONC, silver fulminate; HCNO, fulminic acid),^{1c,2d,4} and there are also theoretical and experimental reports on the corresponding dipseudohalogen (ONC–CNO, cyanogen *N,N'*-dioxide).⁵ The existence of dipseudohalogen species containing cyanate units has also been postulated by several authors;⁶ however, there are no experimental proofs for a compound of the type $\text{N}\equiv\text{C}-\text{O}-\text{O}-\text{C}\equiv\text{N}$ (**1**, oxocyanogen, dioxocyan). In 1980, Delgado and Fernandez reported the formation of oxocyanogen (**1**) as an intermediate species in the reaction of AgOCN with Br_2 .⁷ In that paper, the authors claimed to have stabilized “(OCN)₂” by subsequent reaction with TiCl_4 , resulting in the formation of a polymeric compound of the type $\{\text{TiCl}_4(\text{OCN})_2\}_n$.⁷ However, no direct evidence for the formation of (OCN)₂ was found.

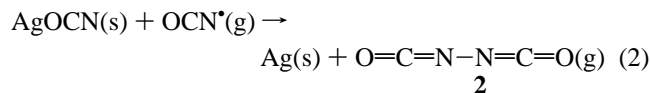
Results and Discussion

We have now carried out a combined theoretical and experimental study and investigated the reaction behavior of AgOCN with Br_2 both in solution and in a neat reaction at room temperature. In this note, we want to report direct evidence for the intermediate formation of $\text{O}=\text{C}=\text{N}-\text{N}=\text{C}=\text{O}$ (**2**,

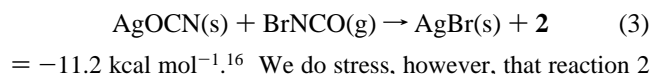
isooxocyanogen, diisooxocyan). It is well established that AgOCN reacts with Br_2 at temperatures as high as 200 °C to form bromine isocyanate, BrNCO, in high yield.⁸ Carbonyl diisocyanate, $\text{CO}(\text{NCO})_2$, is a known side product of this reaction.^{8d,9} In the present study, we reacted a large excess of freshly prepared and thoroughly dried (at 150 °C) AgOCN with Br_2 (distilled and dried over P_4O_{10}) at 18 °C in a gas cell which was especially designed for this experiment.¹⁰ All absorptions in the gas IR spectrum could undoubtedly assigned to carbonyl diisocyanate as the only stable IR-active product in the gas phase (no remaining BrNCO).⁹ Careful analysis of the nonvolatile solid revealed, besides unreacted AgOCN, the presence of AgBr and elemental silver. In another experiment, we repeated the reaction of AgOCN with Br_2 in a stainless steel–glass vacuum line and isolated (volatile at –115 °C) and identified elemental nitrogen as a further product. The formation of N_2 (and not O_2 !) was unequivocally established by gas discharge and mass spectrometry.¹¹ However, traces of CO and of CO_2 were also detected by mass spectrometry. The volumetric analysis revealed that 3–4 equiv of bromine (Br_2) generates 1 equiv of nitrogen (N_2). Therefore, the overall stoichiometry of the reaction can be approximated according to eq 1. According to



eq 1 2.75 equiv Br_2 corresponds to 1 equiv of N_2 . Experimentally it was found that 3–4 equiv of Br_2 generated 1 equiv of N_2 . This may indicate either very crude volumetric data or that eq 1 just gives an approximate overall stoichiometry. Elemental silver may be formed by reaction of OCN^\bullet radicals with AgOCN (eq 2). This reaction was estimated to be thermodynamically



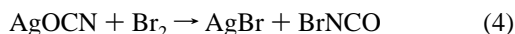
highly favorable: $\Delta H^\circ(2) = -53.7 \text{ kcal mol}^{-1}$.¹² The formation of AgBr can easily be explained by reaction of AgOCN with BrNCO (eq 3), which is thermodynamically allowed by $\Delta H^\circ(3)$



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- (10) Gas IR (10 cm, KBr, 2 Torr, Philips PU9800 FTIR) ν in cm^{-1} : 2275 s, 2242 vs, 1775 s, 1768 sh, 1748 s, 1738 s, 1428 vs, 1405 m, 1075 vs, 1070 vs, 730 m, 725 sh, 618 sh, 609 m; for assignment, see ref 9.
- (11) MS (EI, 70 eV, 20 °C) *m/e* (intensity): 32 (2), 28 (100). Reaction of AgOC^{15}N with Br_2 , MS (EI, 70 eV, 20 °C) *m/e* (intensity): 32 (2), 30 (100), 29 (10), 28 (8).
- (12) $U_L(\text{AgOCN}) = 166.7 \text{ kcal mol}^{-1}$,¹³ $I_P(\text{Ag}) = 175.8 \text{ kcal mol}^{-1}$,¹⁴ $E_A(\text{OCN}) = 83.0 \text{ kcal mol}^{-1}$,¹⁵ $\Delta H_{\text{atom}}(\text{Ag}) = 68.0 \text{ kcal mol}^{-1}$,¹⁴ $\text{BE}(\text{N}-\text{N}) = 59.6 \text{ kcal mol}^{-1}$.¹³
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may not necessarily be valid since reaction 4 followed by



reaction 3 also results in OCNNCO. The formation of substantial amounts of elemental silver, however, can best be explained by a radical mechanism (i.e. eq 2).

We also studied the reaction of AgOCN with Br₂ in solution (CFCl₃, CH₂Cl₂) at various temperatures (−60, −40, 20 °C) and followed the reaction by ¹⁴N NMR spectroscopy. We have found that an equimolar reaction of AgOCN with Br₂ and with an excess of bromine (eq 4) led mainly to the formation BrNCO and AgBr. However, if bromine was reacted with a 10-fold excess of AgOCN, OC(NCO)₂ was observed as the major product.¹⁷ In contrast to an earlier report according to which a solution of oxocyanogen can be filtered at −60 °C⁷ we could not find any evidence for the existence of oxocyanogen (**1**) at this temperature. We therefore rule out the formation of oxocyanogen (**1**) as a reactive intermediate species in the reaction of AgOCN with Br₂. Moreover, the generation of elemental nitrogen can only be explained by the formation of isooxocyanogen, OCN–NCO (**2**), since atomic nitrogen can be ruled out as a high-energy intermediate species.

To explain why isooxocyanogen (**2**) and not oxocyanogen (**1**) is formed as a short-lived intermediate by the reaction of AgOCN with Br₂, we carried out ab initio computations at correlated levels.¹⁸ The structures of both isomers were computed and fully optimized at the MP2(FU)/6-31G(d,p) level of theory (Figure 1). The N–N bound species **2** turned out to be favored over the O–O isomer **1** by 89.9 kcal mol^{−1} at the HF level and by 82.1 kcal mol^{−1} at the MP2 level (Table 1). The very long and weak O–O bond in **1** of 1.62 Å (cf. *d*(O–O, H₂O₂) = 1.47 Å)³ is in contrast to the relatively short N–N bond in **2** of 1.39 Å. The latter value of the N–N distance corresponds to a bond order between a single and a double bond (typical values: N–N single bond, 1.449 Å; N=N double bond, 1.252 Å).¹⁹ With a reported N–N bond dissociation energy for N₂H₄ of 59.6 kcal mol^{−1} (*d*(NN) = 1.45 Å)¹³ and for N₂H₂ of 122 kcal mol^{−1} (*d*(NN) = 1.25 Å),^{19a} we estimate a N–N bond dissociation energy for OCNNCO (**2**) of roughly 79 kcal mol^{−1}. Although the *final* dissociation products of the two isomers **1** and **2** are the same, the difference between the estimated N–N bond dissociation energy for **2** and the energy difference between **1** and **2** (HF 89.9, MP2 82.1 kcal mol^{−1}) can be explained by the initial formation of the high-energy •OCN radical in the dissociation of **1** which has to rearrange to give the more stable OCN• radical. This rather special bonding situation can be rationalized in the NBO picture by strong noncovalent contributions (donor–acceptor interaction, negative hyperconjugation).^{18,20,21} In the case of the O–O compound (**1**), there are two strong intramolecular donor–acceptor interactions which both weaken the O–O bond and therefore also explain the long O–O distance. In one interaction electron density is transferred from the bonding π(CN) orbitals into the empty and antibonding σ*(OO) orbital (Figure 2 (top)). In the

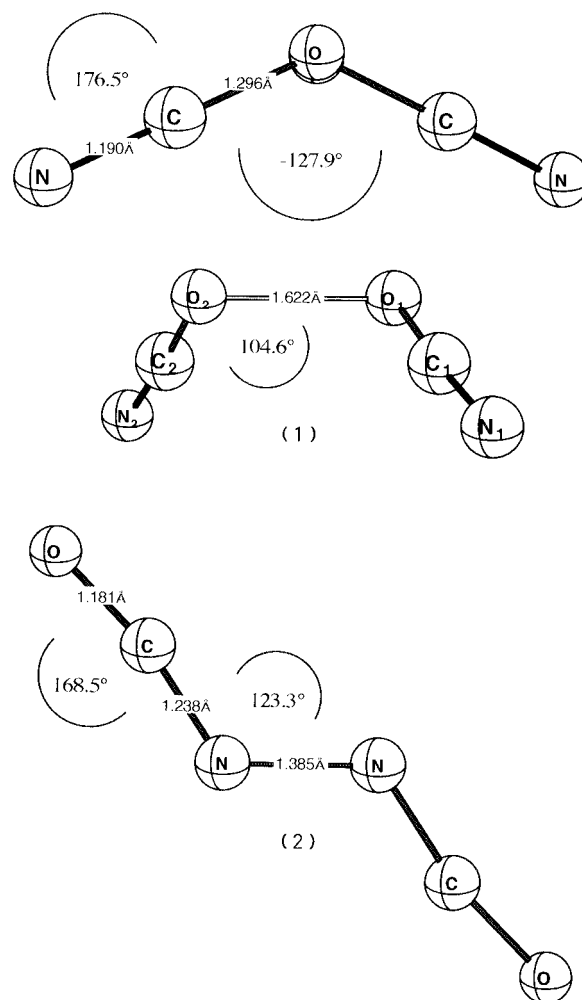


Figure 1. MP2-optimized structures: (top) two different views of NCO–OCN (**1**); (bottom) OCN–NCO (**2**).

Table 1. Ab Initio Data (MP2(FU)/6-31G(d,p) Level) for Oxocyanogen, NCO–OCN (**1**), and Isooxocyanogen, OCN–NCO (**2**)

	N≡C–O–O–C≡N (1)	O=C=N–N=C=O (2)
<i>E</i> /au	−335.103 436 5	−335.234 22
<i>E</i> _{rel} /kcal mol ^{−1}	82.9	0.00
symmetry	<i>C</i> ₂	<i>C</i> _{2h}
<i>d</i> (OO)/Å	1.622	
<i>d</i> (NN)/Å		1.385
<i>d</i> (OC)/Å	1.296	1.181
<i>d</i> (CN)/Å	1.190	1.238
∠(COOC)/deg	127.9	
∠(NCOO)/deg	−175.9	
∠(OCNN)/deg		180.0
∠(CNNC)/deg		180.0
∠(NCO)/deg	176.5	168.5
∠(COO)/deg	104.6	
∠(CNN)/deg		123.3

other interaction, electron density flows from the occupied σ*(OO) orbital into the empty and antibonding π*(CN) orbitals (Figure 2 (bottom)). In contrast to this situation, the N–N compound (**2**) only shows one strong hyperconjugation with a donation of electron density from the π(C1N1) orbital into the π*(C2N2) orbital [and vice versa: π(C2N2) → π*(C1N1)]. This interaction clearly strengthens the N–N bond (Figure 3) and therefore accounts for a partial-double-bond character of the N–N bond.

In VB terms^{22,23} the preference for the N–N bound isomer **2** over the O–O compound **1** can be explained either by the

(17) ¹⁴N NMR (14.462 MHz, NS = 40,000, PW = 48 μs, Bruker SY 200), δ in ppm relative to MeNO₂: BrNCO, −393.1 (Δ*ν*_{1/2} = 220 Hz); OC(NCO)₂, −317.7 Hz (Δ*ν*_{1/2} = 360 Hz).

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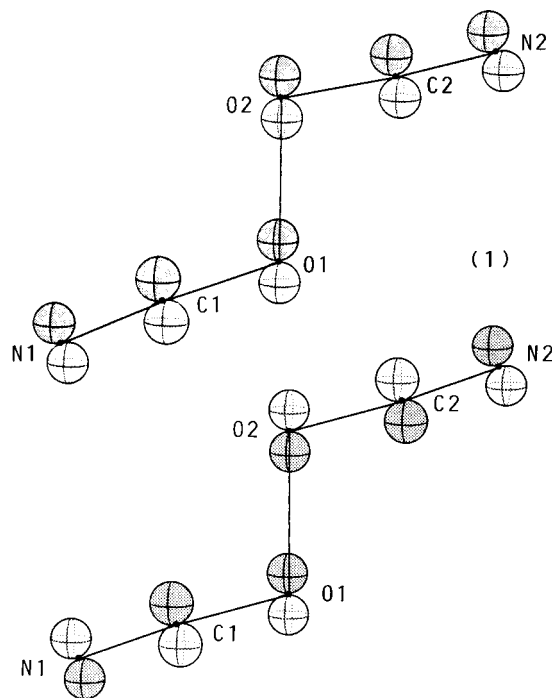


Figure 2. Hyperconjugation in NCO-OCN (**1**): (top) $\pi(\text{CN}) \rightarrow \sigma^*(\text{OO})$, $2 \times 20 \text{ kcal mol}^{-1}$; (bottom) $\sigma(\text{OO}) \rightarrow \pi^*(\text{CN})$, 16 kcal mol^{-1} .

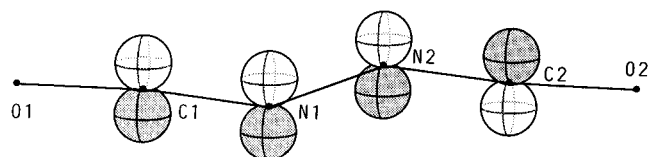


Figure 3. Hyperconjugation in OCN-NCO (**2**): $\pi(\text{C1N1}) \rightarrow \pi^*(\text{C2N2})$ (same for $\pi(\text{C2N2}) \rightarrow \pi^*(\text{C1N1})$), $2 \times 11 \text{ kcal mol}^{-1}$.

preferred localization of the single electron in the radical intermediate OCN^* in a nitrogen AO or by the fact that lone pair-lone pair repulsion favors compound **2** (one LP per N atom) over compound **1** (two LPs per O atom) (cf. dissociation energies: $\text{HO}-\text{OH}$, $34.5 \text{ kcal mol}^{-1}$; $\text{H}_2\text{N}-\text{NH}_2$, $59.1 \text{ kcal mol}^{-1}$).^{13,14} The calculated geometry for the OCN^* radical ($d(\text{NC}) = 1.23 \text{ \AA}$, $d(\text{CO}) = 1.13 \text{ \AA}$)²⁴ is also in better accord

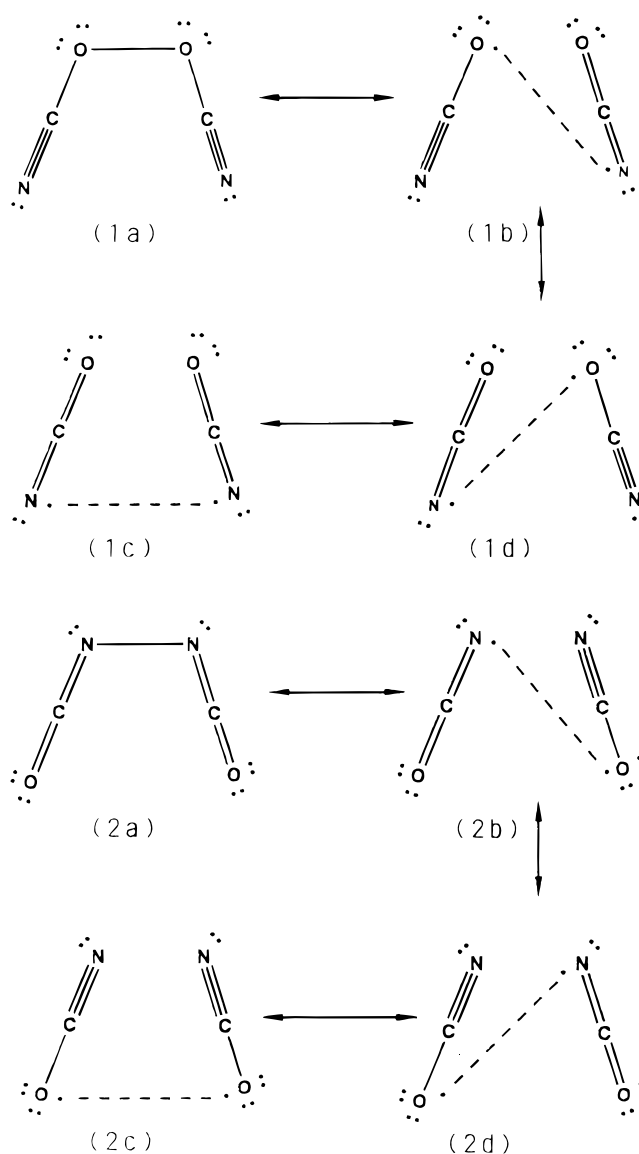


Figure 4. Lewis structures for NCO-OCN (**1**) and OCN-NCO (**2**). with a Lewis structure of type **A** than with one of type **B**. These



considerations clearly suggest that structure **2a** should be preferred over structure **1a**, i.e. OCN-NCO (**2**) rather than NCO-OCN (**1**) (Figure 4).

Nicely in agreement with this, MO computations for the NCO radical clearly indicate much larger odd-electron density for nitrogen (0.6477) than for oxygen (0.0994).²⁴

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$$E_{\varphi\varphi^*}^{(2)} = -2 \frac{\langle \varphi | h^F | \varphi^* \rangle^2}{E_{\varphi^*} - E_{\varphi}}$$

with h^F being the Fock operator.

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