*Inorg. Chem.* **1996,** *35,* 4791−4793

# Does Diisooxocyan (OCN−NCO) Exist?

**Axel Schulz and Thomas M. Klapötke***

Department of Chemistry, University of Glasgow,
Glasgow G12 8QQ, U.K.

*Received January 17, 1996*

## Introduction

The linear cyanate ion $[NCO]^-$ 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).[1ac,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 $[CNO]^-$ 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 N≡C−O−O−C≡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 $\{TiCl_4(OCN)_2\}_n$.[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 O═C═N−N═C═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, $CO(NCO)_2$, 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

$$24\mathrm{AgOCN} + 11\mathrm{Br}_2 \rightarrow 22\mathrm{AgBr} + 2\mathrm{Ag} + 8\mathrm{OC(NCO)}_2 + 4\mathrm{N}_2 \quad (1)$$

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

$$\mathrm{AgOCN(s)} + \mathrm{OCN}^\bullet\mathrm{(g)} \rightarrow \mathrm{Ag(s)} + \underset{\mathbf{2}}{\mathrm{O{=}C{=}N{-}N{=}C{=}O}}\mathrm{(g)} \quad (2)$$

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

$$\mathrm{AgOCN(s)} + \mathrm{BrNCO(g)} \rightarrow \mathrm{AgBr(s)} + \mathbf{2} \quad (3)$$

$= -11.2\ \mathrm{kcal\ mol^{-1}}$.[16] We do stress, however, that reaction 2

---

(1) (a) Defrees, D. J.; Loew, G. H.; McLean, A. D. *Astrophys. J.* **1982**, *254*, 405. (b) Yokoyama, K.; Takane, S.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2230. (c) Pinnavaia, N.; Bramley, M. J.; Su, M. D.; Green, W. H.; Handy, N. C. *J. Mol. Phys.* **1993**, *78*, 319. (d) East, A. L. L.; Johnson, C. S.; Allen, W. D. *J. Chem. Phys.* **1993**, *98*, 1299. (e) Blanch, R. J.; McCluskey, A. *Chem. Phys. Lett.* **1995**, *241*, 116.

(2) (a) Breulet, J.; Lievin, J. *Theor. Chim. Acta* **1982**, *61*, 59. (b) Fusina, L.; Carlotti, M.; Carli, B. *Can. J. Phys.* **1984**, *62*, 1452. (c) Spiglanin, T. A.; Chandler, D. W. *J. Chem. Phys.* **1987**, *87*, 1577. (d) Hop, C. E. C. A.; Vandenberg, K. J.; Holmes, J. L.; Terlouw, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 72. (e) Yamada, K. M. T.; Winnewisser, M.; Johns, J. W. C. *J. Mol. Spectrosc.* **1990**, *140*, 353. (f) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *100*, 4498. (g) Boyce, C. W.; Gillies, C. W.; Warner, H.; Gillies, J. Z.; Lovas, F. J.; Suenram, R. D. *J. Mol. Spectrosc.* **1995**, *171*, 533. (h) Brown, S. S.; Berghout, H. J.; Crim, F. F. *J. Chem. Phys.* **1995**, *102*, 8440.

(3) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, **1984,** p 336.

(4) (a) Winnewisser, M.; Bodenseh, H. K. *Z. Naturforsch.* **1967**, *22A*, 1724. (b) Winnewisser, B. P.; Jensen, P. *J. Mol. Spectrosc.* **1983**, *101*, 408. (c) Quapp, W.; Albert, S.; Winnewisser, B. P.; Winnewisser, M. *J. Mol. Spectrosc.* **1993**, *160*, 540. (d) Wagner, G.; Winnewisser, B. P.; Winnewisser, M.; Sarka, K. *J. Mol. Spectrosc.* **1993**, *162*, 82. (e) Islami, K.; Jabs, W.; Preusser, J.; Winnewisser, M.; Winnewisser, B. P. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1995**, *99*, 565.

(5) (a) Grundmann, C. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 260. (b) Maier, G.; Teles, J. H. *Angew. Chem.* **1987**, *99*,152; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 155. (c) Pasinszki, T.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1995**, *117*, 8425.

(6) (a) Hunt, H. *J. Am. Chem. Soc.* **1932**, *54*, 907. (b) Powell, P.; Timms, P. *TheChemistry of Non-Metals*; Chapman and Hall: London, 1974.

(7) Delgado, M. S.; Fernandez, V. *Z. Anorg. Allg. Chem.* **1981**, *476*, 149.

(8) (a) Gottardi, W. *Angew. Chem.* **1971**, *83*, 445; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 416. (b) Gottardi, W. *Monatsh. Chem.* **1972**, *103*, 1150. (c) Frost, D. C.; MacDonald, C. B.; McDowell, C. A.; Westwood, N. P. C. *Chem. Phys.* **1980**, *47*, 111. (d) Devore, T. C. *J. Mol. Spectrosc.* **1987**, *162*, 287. (e) Gerke, M.; Schatte, G.; Willner, H. *J. Mol. Spectrosc.* **1989**, *135*, 359.

(9) Balfour, W. J.; Fougere, S. G.; Klapstein, D.; Nau, W. M. *Spectrochim. Acta* **1994**, *50A*, 1039.

(10) Gas IR (10 cm, KBr, 2 Torr, Philips PU9800 FTIR) $\nu$ in $\mathrm{cm^{-1}}$: 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) $U_L(\mathrm{AgOCN}) = 166.7\ \mathrm{kcal\ mol^{-1}}$,[13] $I_P(\mathrm{Ag}) = 175.8\ \mathrm{kcal\ mol^{-1}}$,[14] $E_A(\mathrm{OCN}) = 83.0\ \mathrm{kcal\ mol^{-1}}$,[15] $\Delta H_{\mathrm{atom}}(\mathrm{Ag}) = 68.0\ \mathrm{kcal\ mol^{-1}}$,[14] BE(N−N) $= 59.6\ \mathrm{kcal\ mol^{-1}}$.[13]

(13) Klapötke, T. M.; Tornieporth-Oetting, I. C. *Nichtmetallchemie*; VCH: Weinheim, Germany, 1994; pp 81, 93, and 96−103 and Appendix.

(14) Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*; Cambridge University Press: Cambridge, U.K., 1982; Appendix.

(15) Ziegler, T.; Gutsev, G. L. *J. Comput. Chem.* **1992**, *13*, 70.

(16) (a) See ref 12; BE(Br−N) $= 46.9\ \mathrm{kcal\ mol^{-1}}$,[13,16b] $E_A(\mathrm{Br}) = 82.7\ \mathrm{kcal\ mol^{-1}}$,[13] $U_L(\mathrm{AgBr}) = 179.2\ \mathrm{kcal\ mol^{-1}}$.[13] (b) Schulz. A.; Tornieporth-Oetting, I. C.; Klapötke, T. M. *Inorg. Chem.* **1995**, *34*, 4343.

S0020-1669(96)00049-3 CCC: $12.00

may not necessarily be valid since reaction 4 followed by

$$\mathrm{AgOCN} + \mathrm{Br_2} \rightarrow \mathrm{AgBr} + \mathrm{BrNCO} \qquad (4)$$

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 $Br_2$ in solution ($CFCl_3$, $CH_2Cl_2$) at various temperatures (−60, −40, 20 °C) and followed the reaction by $^{14}N$ NMR spectroscopy. We have found that an equimolar reaction of AgOCN with $Br_2$ 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 °C[7] 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 $Br_2$. 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 $Br_2$, 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, $H_2O_2$) = 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 $N_2H_4$ of 59.6 kcal $mol^{-1}$ ($d$(NN) = 1.45 Å)[13] and for $N_2H_2$ 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 $^{\bullet}$OCN radical in the dissociation of **1** which has to rearrange to give the more stable OCN$^{\bullet}$ 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 $\pi$(CN) orbitals into the empty and antibonding $\sigma^*$(OO) orbital (Figure 2 (top)). In the other interaction, electron density flows from the occupied $\sigma$(OO) orbital into the empty and antibonding $\pi^*$(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 $\pi$(C1N1) orbital into the $\pi^*$(C2N2) orbital [and vice versa: $\pi(\mathrm{C2N2}) \rightarrow \pi^*(\mathrm{C1N1})$]. This interaction clearly strengthens the N−N bond (Figure 3) and therefore accounts for a partial-double-bond character of the N−N bond.

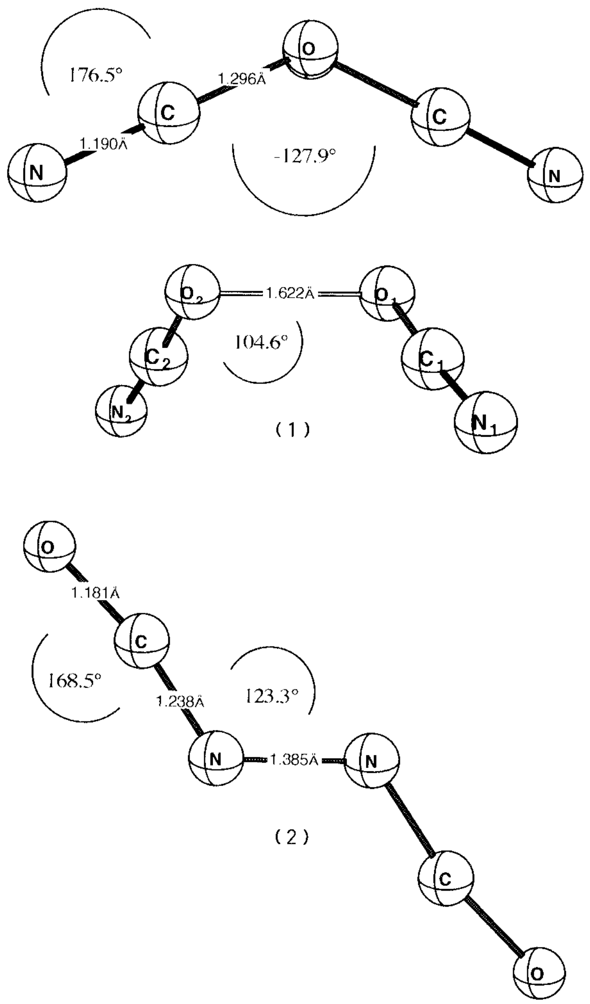

**Figure 1.** MP2-optimized structures: (top) two different views of NCO−OCN (**1**); (bottom) OCN−NCO (**2**).

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

| | N≡C−O−O−C≡N (**1**) | O=C=N−N=C=O (**2**) |
|---|---|---|
| $E$/au | −335.103 436 5 | −335.234 22 |
| $E_{rel}$/kcal $mol^{-1}$ | 82.9 | 0.00 |
| symmetry | $C_2$ | $C_{2h}$ |
| $d$(OO)/Å | 1.622 | |
| $d$(NN)/Å | | 1.385 |
| $d$(OC)/Å | 1.296 | 1.181 |
| $d$(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 |

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] $^{14}N$ NMR (14.462 MHz, NS = 40.000, PW = 48 $\mu$s, Bruker SY 200), $\delta$ in ppm relative to $MeNO_2$: BrNCO, −393.1 ($\Delta\nu_{1/2}$ = 220 Hz); $OC(NCO)_2$, −317.7 Hz ($\Delta\nu_{1/2}$ = 360 Hz).

[18] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, K.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

[19] (a) Janoschek, R. *Angew. Chem.* **1993**, *105*, 242; *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 230. (b) Holleman, A. F.; Wiberg, E; Niberg, N. *Lehrbuch der Anorganischen Chemie*; Walter de Gruyter: Berlin, New York, 1985; pp 562−563.

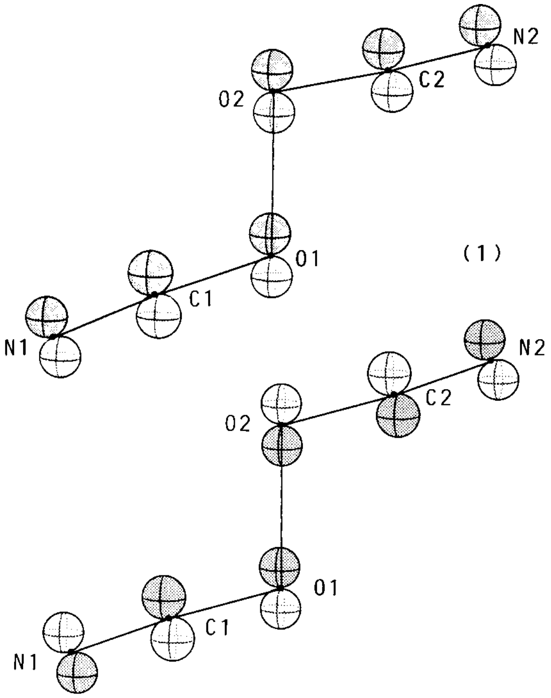

**Figure 2.** Hyperconjugation in NCO−OCN (**1**): (top) $\pi$(CN) → $\sigma^*$(OO), 2 × 20 kcal mol$^{-1}$; (bottom) $\sigma$ (OO) → $\pi^*$(CN), 16 kcal mol$^{-1}$.

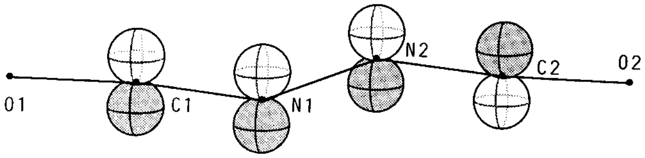

**Figure 3.** Hyperconjugation in OCN−NCO (**2**): $\pi$(C1N1) → $\pi^*$(C2N2) (same for $\pi$(C2N2) → $\pi^*$(C1N1)), 2 × 11 kcal mol$^{-1}$.

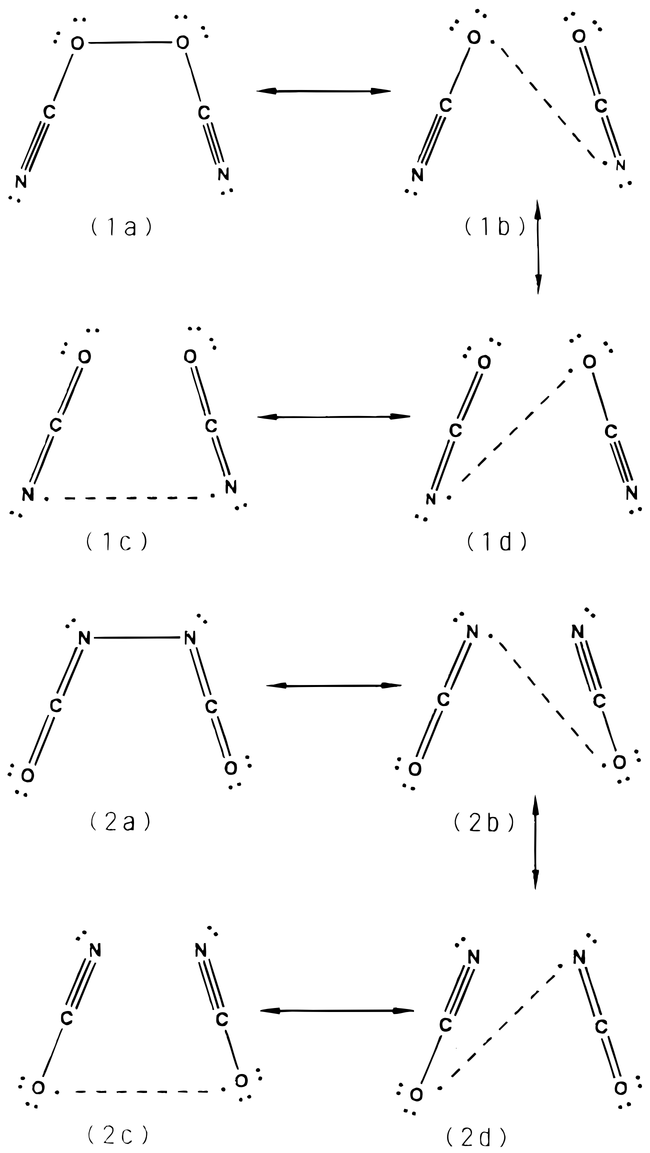

**Figure 4.** Lewis structures for NCO−OCN (**1**) and OCN−NCO (**2**).

preferred localization of the single electron in the radical intermediate OCN$^\bullet$ 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: HO−OH, 34.5 kcal mol$^{-1}$; $H_2N{-}NH_2$, 59.1 kcal mol$^{-1}$).[13,14] The calculated geometry for the OCN$^\bullet$ radical ($d$(NC) = 1.23 Å, $d$(CO) = 1.13 Å)[24] is also in better accord 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]

**Acknowledgment.** The financial support of this research by the DFG and the University of Glasgow is gratefully acknowledged. We are also indebted to Jim Gall for recording the $^{14}$N NMR spectra and to Prof. Richard D. Harcourt for initiating suggestions and many helpful discussions. We thank both reviewers for most valuable comments and suggestions.

IC960049Z

---

(20) (a) Reed, A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Reed, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7362. (c) Reed, A.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969. (d) NBO analysis: In the quantum mechanical computation (subjecting the HF density matrix as represented in the localized NBOs to a second-order perturbative analysis), the energy was computed according to

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

with $h^{\mathrm{F}}$ being the Fock operator.

(21) Klapötke, T. M.; Schulz, A. *Quantenchemische Methoden in der Hauptgruppenchemie*; Spektrum: Heidelberg, Germany, 1996; p 101.

(22) Harcourt, R. D. Qualitative Valence-Bond Descriptions of Electron-Rich Molecules: Pauling "3-Electron Bonds" and "Increased-Valence" Theorie. In *Lecture Notes in Chemistry*; Berthier, G., Dewar, M. J. S., Fischer, H., Fukui, K., Hall, G. G., Hartmann, H., Jaffé, H. H., Jortner, J., Kutzelnigg, W., Ruedenberg, K., Scrocco, E., Eds.; Springer: Berlin, Heidelberg, New York, 1982.

(23) Harcourt, R. D. In *Valence bond theory and chemical structure*; Klein, D. J., Trinajstic, N., Eds.; Elsevier: Amsterdam, 1990; p 251.

(24) Thomson, C.; Wishart, B. J. *Theor. Chim. Acta* **1974**, *35*, 361.