J. Org. Chem. **1994**, *59*, 3237-3239

A Theoretical Study of Two Forms of NCNCHCl and Their Interconversion, Relative Energies, and Infrared Spectra[†]

Per N. Skancke

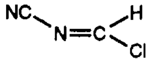
Department of Chemistry, The University of Tromsø, N-9037 Tromsø, Norway

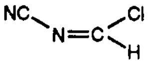
Received January 25, 1994

Introduction

In a very recent paper the reaction between isocyanogen, CNCN, and HCl was studied both in the condensed and in the vapor phase.[1] In order to compete with polymerization reactions of the very unstable and reactive isocyanogen the reactions with HCl were performed at very low temperatures, and products of the type NCNCHCl were identified and characterized by means of NMR and high-resolution mass spectroscopy.

The product of the reaction may appear in the two different isomeric forms





However, the observed ^1H and ^{13}C NMR spectra of the product showed only one signal even at very low temperatures (*i.e.*, −85 °C).

Several possible interpretations of the recorded single-signal spectra were suggested in the paper[1] referred to above: (a) The NCNC skeleton in the product is roughly linear even if imines normally are bent. (b) There is an accidental coincidence between the signal for the two different stereoisomers shown above. (c) There is an equilibrium between the two forms which is rapidly established on the NMR time scale. In the paper referred to above the last of the three alternatives was favored.[1] This implies that the height of the barrier for cis–trans isomerization will be of crucial importance for the interpretation of the NMR spectra.

The present paper presents the results of ab initio calculations including electron correlation aiming at elucidating the equilibrium structures of the two stereoisomers, their relative energies, and the nature and energy of the transition state connecting them. Predicted IR transitions of the two isomers are also included and compared with a spectrum recorded in the gas phase.[1]

Computations

The species HCl, NCNC (**1**), the product forms **2a** and **2b**, and the transition state (**TS**) connecting them through an inversion barrier were fully geometry optimized by RHF calculations using the 6-31G** basis.[2] All stationary points on the potential surfaces were characterized by analytically calculated vibrational frequencies using the same basis. Energies in the stationary points were calculated using QCISD(T)[3] calculations and the same basis. All calculations were performed by the program Gaussian 92.[4]

Results and Discussion

The optimized equilibrium structures shown in Figure 1 demonstrate that isocyanogen (**1**) is a linear molecule having terminal C–N bonds that are very short and roughly equal. The two different isomers of the reaction product, *viz.* **2a** and **2b**, are both planar. The isomer having Cl in the cis-position to the cyano group (**2a**) has a C=N–C angle of 122°, whereas the other isomer (**2b**) has a corresponding angle of 117°; *i.e.*, both forms are definitely nonlinear. This rules out alternative (a) in the interpretation of the observed NMR spectra.

The relative energies, given in Table 2, show that the reaction energy is predicted to be 16 kcal/mol when ZPE corrections are included. Furthermore, we predict an energy difference of 1.6 kcal/mol between the two stereoisomers **2a** and **2b**, the former being the more stable one. This value is somewhat larger than the difference in heats of formation at 298 K (0.7 kcal/mol) previously predicted by MNDO/PM3 calculations.[5] Our predicted entropies are 0.071 kcal/mol K for both of the isomers. Thus, the small energy difference found would imply that none of the isomers should be ruled out with reference to thermodynamics and that the possibility of an equilibrium between them is dependent on the height of the barrier to interconversion. We have optimized the transition state for such a conversion. Its structure, given in Figure 2, shows a virtually linear NCNC moiety, confirming a cis–trans isomerization through inversion. The normal mode associated with the single imaginary frequency of 281*i* cm^{-1} is an in-plane bending vibration of the valence angle around the imine nitrogen (angle C_2–N_3–C_4). Our predicted barrier, corrected for ZPE, is 17.7 kcal/mol relative to the most stable isomer (**2a**). This value is lower than the one of 23 kcal/mol reported using MNDO/PM3.[1] We believe that our predicted value is a realistic one as all the species involved have stable RHF solutions, reducing the importance of correlation energy corrections to relative energies. Furthermore, the basis set applied contains polarization functions on all atoms, and the size-consistent CI method chosen contains corrections also for triple excitations. The barrier predicted is expected to be too low in order to prevent an establishment of a thermal equilibrium between the isomers **2a** and **2b**. This implies that none of the isomers is preserved by a high isomerization barrier. This conclusion is consistent with the assignment of the observed IR spectrum discussed below (vide infra). A search for an alternative TS related to a rotation around the N_3–C_4 bond was also attempted. This

---

[†] Dedicated to Professor Dr. W. Lüttke, Universität Göttingen, on the occasion of his 75th birthday.

(1) Goede, S. J.; van Baar, B. L. M.; Bickelhaupt, F. *J. Org. Chem.* **1993**, *58*, 6930.

(2) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(3) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(4) Gaussian 92, Revision A: 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, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. J.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J.; Pople, J. A. Gaussian, Inc., Pittsburg PA, 1992.

(5) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

0022-3263/94/1959-3237$04.50/0

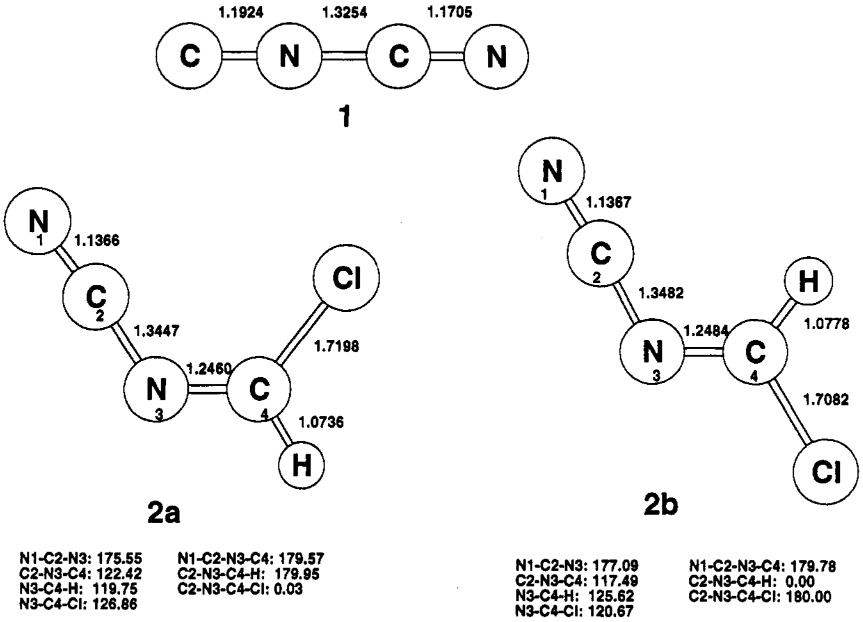


Figure 1. Fully optimized geometries of the parent compound NCNC and the two stereoisomers of the addition product. Optimizations at RHF/6-31G** level.

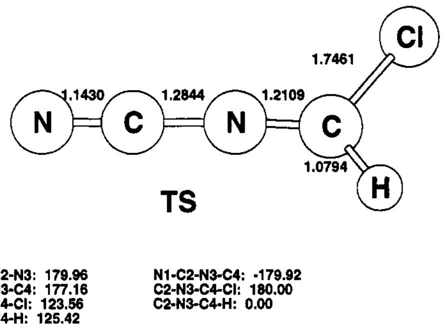


Figure 2. Fully optimized geometry of the transition state for the interconversion of the stereoisomers **2a** and **2b**. Optimization at RHF/6-31G** level.

Table 1. Total Energies (au) and ZPE (kcal/mol) at SCF Level for the Species Shown in Figures 1 and 2. All Geometries Optimized by RHF/6-31G**

	SCF	QCISD(T)	ZPE
HCl	-460.066 214	-460.224 539	4.54
NCNC (1)	-184.557 249	-185.144 728	10.25
NCNC-HCl (**2a**)	-644.654 131	-645.404 756	21.02
NCNC-HCl (**2b**)	-644.653 150	-645.401 704	20.72
NCNC-HCl (**TS**)	-644.625 000	-645.375 008	20.05

Table 2. Energies (kcal/mol) Relative to E(HCl) + E(1) without and with ZPE Corrections. Basis Set 6-31G**

	SCF	QCISD(T)	ΔZPE	QCISD(T) + ΔZPE
E(HCl) + E(1)	0.0	0.0	0.0	0.0
ΔE(**2a**)	-19.24	-22.27	6.23	-16.04
ΔE(**2b**)	-18.63	-20.35	5.93	-14.42
ΔE(**TS**)	0.96	-3.60	5.26	1.66

Table 3. Calculated Vibrational Frequencies (cm^{-1}) and Infrared Intensities (KM/mol) for the Species 2a and 2b. Basis Set 6-31G. Predicted Frequencies Scaled by 0.89. Observed Gas-Phase Spectrum Included for Comparison**

2a			2b			
freq.	int.	mode	freq.	int.	mode	expl[a]
134	1	in-plane bd.	163	16	out-of-plane bd.	
293	0	out-of-plane bd.	164	8	in-plane bd.	
412	12	in-plane bd.	380	1	in-plane bd.	
590	21	out-of-plane bd.	523	14	out-of-plane bd.	
657	3	in-plane bd.	551	23	in-plane bd.	
773	93	in-plane bd.	868	125	in-plane bd.	801
930	6	out-of-plane bd.	971	8	out-of-plane bd.	889
939	60	in-plane bd.	989	10	in-plane bd.	949
1324	31	in-plane bd.	1327	31	in-plane bd.	
1689	322	N_2–C_4 str.	1669	405	N_2–C_4 str.	1625
2318	83	C_2–N_1 str.	2317	121	C_2–N_1 str.	2220
3026	2	C–H str.	2978	2	C–H str.	3120

[a] Reference 1.

was carried out by relaxing all structural parameters except for the valence angles around the imine nitrogen which was kept fixed at a value of 120°. The optimization of the otherwise fully relaxed structure led to a CHCl moiety roughly orthogonal to the plane through NCNC. In this stationary point there was a substantial residual force on the imine valence angle tending to open this angle toward a linear NCNC framework and, thus, coinciding with the TS for inversion. The normal mode associated with the single imaginary frequency of 596i cm^{-1} is dominated by a twist of the CHCl moiety combined with a bending of the imine valence angle. The force constant matrix also revealed a coupling of these two deformations. At the RHF level the energy (without ZPE corrections) of this constrained stationary point is found to be 20.3 kcal/mol above the fully optimized TS for inversion.

In order to provide information needed for disentangling the recorded IR transitions of the reaction product we have calculated analytically the vibrational spectra of both isomers. The predicted frequencies and intensities associated with the 12 normal modes are given in Table 3 together with six bands observed[1] in the gas phase. In order to compensate for lack of anharmonicity and electron correlation corrections, we have scaled the predicted frequencies by a factor of 0.89. As revealed in Table 3 the predicted stretching frequencies at around 3000, 2300, and 1670 cm^{-1} for both isomers match the three observed high-frequency bands rather well. It is worth noting that a predicted in-plane vibration at around 1320 cm^{-1} in both isomers does not correspond to any band in the experimental spectrum. A reasonable assignment of the three observed bands at 801, 889, and 949 cm^{-1} would be to link the lowest one to the in-plane bending absorption at 773 cm^{-1} for isomer **2a**, the next one to the in-plane bending absorption at 868 cm^{-1} for isomer **2b**, and the final one to the predicted contributions both from the 930 and 939 cm^{-1} absorptions of **2a** and the corresponding absorptions of **2b** at 971 and 989 cm^{-1}. This assignment of the observed IR bands gives strong support for assuming that both isomers are present in significant amounts in the reaction product.

Acknowledgment. The calculations have been partially carried out on CRAY at the SINTEF Supercomputing Center, Trondheim, Norway. The author thanks the Norwegian Research Council for granting CPU time on this computer.