Crystal and Molecular Structure of 3-Iodo-2-propynyl-N-butylcarbamate

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Z. Naturforsch. 52 b, 256–258 (1997); received October 15, 1996

Complexes of Iodo-Acetylenes, X-Ray

The crystal structure of the title compound has been determined by X-ray diffraction methods. Due to the Lewis acidic character of the iodine substituent a “zig-zag” chain is formed via intermolecular interactions (2.933(4) Å) between iodine and oxygen atoms of the carbamate moiety. A three-dimensional network is formed through hydrogen-bridging (2.04 Å) between NH-groups and the oxygen atoms of the neighboring carbamate group of the next molecule.

1. Introduction

Halogen substituents in some carbon-halogen compounds show a weak electron-deficient character, thus adopting the role of Lewis acid centers, e. g. carbon tetrahalides CX₄ (X = Cl, Br, I) form adducts with other halide anions [1]. This was also reported for iodo- and bromoacetylenes where phosphonium and ammonium salts were used as sources of halide anions [2–4]. However, there are only two reports on adducts of Lewis acidic carbonhalide derivatives with oxygen atoms as Lewis base, viz. [1,4-dioxane-I-C≡C-I] and [cyclohexane-1,4-dione-I-C≡C-I] [5,6].

In this paper we present the X-ray crystal structure investigation of 3-iodo-2-propynyl-N-butylcarbamate (1), a compound that contains both a Lewis acid (I-C≡C-R) as well as a Lewis base center (C=O) in the same molecule.

2. Results and Discussion

Compound 1 crystallizes in the space group P2₁/c with four formula units in the unit cell. The molecular structure of 1 is shown in Fig. 1, important intra- and intermolecular distances and angles are summarized in Tab. I.

Regarding a separate molecule of 1, no unusual structural features are observed: the bond distance I(1)-C(1) of 2.006(6) Å is in good agreement with those reported for other iodoalkynes, viz.

![Fig. 1. Hydrogen-bridging in 1 (thermal ellipsoids at the 50% probability level). Hydrogen atoms except for H(1) and H(1A) are omitted for clarity.](image)

Table I. Selected bond lengths [Å] and angles [°] for 1.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(1)-C(1)</td>
<td>2.006(6)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.183(8)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.440(8)</td>
</tr>
<tr>
<td>N(1)-H(1)</td>
<td>1.00(9)</td>
</tr>
<tr>
<td>I(1B)-O(2A)</td>
<td>2.933(4)</td>
</tr>
<tr>
<td>O(2)-H(1A)-N(1A)</td>
<td>144(6)</td>
</tr>
</tbody>
</table>

2.02 - 2.04 Å [3, 4 and references cited therein]. The angles C(2)-C(1)-I(1) of 177.4(6)° and C(1)-C(2)-C(3) of 175.1(6)° indicate only a slight distortion of the I-C≡C-CH₂ moiety.

An intermolecular hydrogen-bond N(1A)-H(1A)-O(2) is found with a distance H(1A)-O(2) of 2.04(9) Å and an angle N(1A)-H(1A)-O(2) of 144(6)°. This interaction is the reason for the formation of a chain structure along the crystallographic “a”-axis. Another weak inter-
action can be visualized via I···O-contacts (Fig. 2), which also results in the formation of intermolecular chains perpendicular to the “a”-axis forming a three-dimensional network structure. The intermolecular I···O distance, 2.933(4) Å, is considerably shorter than the sum of the van-der-Waals radii of oxygen and iodine (3.5 Å [7]). These contacts are identical with those reported for [cyclohexane-1,4-dione-I-C=C-I] (2.94 Å [6]) and are longer than in the 1,4-dioxane-diidoacetylene adduct (2.65 Å [5]), which is in accord with the stronger basic properties of 1,4-dioxane compared to cyclohexane-1,4-dione.

In summary, the structure of 1 represents a further example of a carbon-halogen compound with a Lewis acid halogen center. The presence of both a Lewis acid and base center in one molecule in combination with an “NH” functionality provides the possibility for the formation of a three-dimensional network structure via short I···O contacts and hydrogen-bridge bonds.

3. Experimental Section

X-ray structure determination of 1

Experimental data of the crystal structure investigation are given in Table II [10]. Our sample of 1 was a gift of “G + G International Inc.”. Suitable crystals were grown by slow evaporation of solvent from a benzene solution of 1 at room temperature. A slightly yellow specimen was fixed onto a glass fiber and investigated on an Enraf Nonius CAD4 four-circle diffractometer at -50 °C. The structure was solved by direct methods using SHELXTL (version 5.0) software [8]. All non-hydrogen atoms were refined anisotropically by least-squares procedures against F² with SHELXL-93 program [9]. The positions of hydrogen atoms were localized from the difference Fourier-map and refined in isotropic approximation except for the hydrogen atoms at C(8); the latter were treated as idealized contributions with d(C-H) = 0.96 Å and Uiso(H) = 1.5Uiso of the parent carbon atom. Additionally, an absorption correction based on ψ-scans was applied to the data set. Final refinement cycles led to convergence with the following residuals: R₁ = 3.07% and wR2(all data) = 8.60%.

Acknowledgements

Support by the Fonds der Deutschen Chemischen Industrie (VCI) for J. L. and by the “Graduiertenkolleg Metallorganische Chemie” of the Philipps-University of Marburg for E. V. A. is gratefully acknowledged. We thank H. Donath for providing suitable crystals for diffractometric measurements.
[10] Further information on the crystal structure determination can be obtained from the Fachinformationzentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the registration number CSD-406184.