

Molecular geometry and optical activity of helically chiral *N*-nitrosamines derived from 1,2,3,4-tetrahydro- and 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline



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ARTICLE INFO

Article history:

Received 4 April 2015

Accepted 13 April 2015

Available online 12 May 2015

ABSTRACT

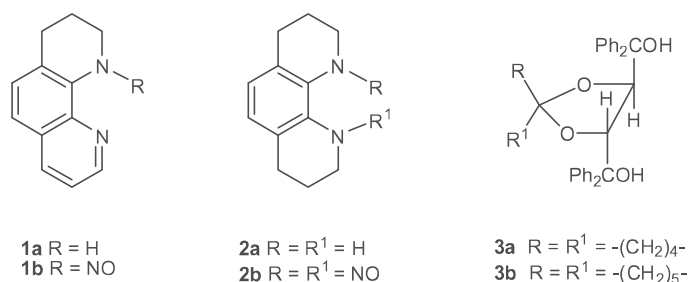
X-ray crystallographic analysis of the title *N*-nitrosamines revealed that they assume helical conformations in the solid state. Nitrosamines **1b** and **2b** were resolved by inclusion crystallization with optically active diols (TADDOLs). The absolute configuration of the guest molecules in the complexes **1b-3b** and **2b-3b** was assigned as *M*. The optical activity of the resolved compounds is manifested by their solid state CD spectra, which showed relatively strong Cotton effects in the region of the nitrosamine $n-\pi^*$ transition. Theoretical calculations of the electronic and CD spectra performed by classic ab initio methods predicted the correct Cotton effect signs of **1b** and **2b**.

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1. Introduction

The chemistry and biological activity of *N*-nitrosamines are the subject of continuing interest with regard to their strong carcinogenic and mutagenic properties.¹ Thus numerous experimental and theoretical investigations have been directed toward establishing their structure–activity relationship.² Their stereochemistry has been thoroughly investigated since it is of primary importance for biological activity.³ The molecular geometry of these compounds is influenced by a partial double bond character between the adjacent nitrogen atoms, which results in restricted rotation about the N–N bond. Since the corresponding energy barrier is relatively high (23–25 kcal/mol), this rotation is very slow at ambient temperatures.⁴ A substitution of the nitroso group at the nitrogen atom of the secondary amines lowers their symmetry, which in the absence of any improper symmetry axis leads to molecular chirality. Owing to a weak long-wavelength absorption near 370 nm, these are attractive models for chiroptical studies.⁵ Thus many optically active compounds of this class have been prepared in order to correlate their optical activity with molecular geometry and also as potential chiral auxiliaries for asymmetric synthesis. Most of these compounds are derived from optically active amines but some of them owe their chirality solely to the hindered rotation about the N–N bond. In the last case, their

optical activity was preserved only in the solid state and upon dissolution rapid racemization occurred.



Continuing our interest on configurationally labile compounds,^{6,7} we turned our attention to derivatives of 1,2,3,4-tetrahydro-1,10-phenanthroline **1a** and 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline **2a**. Both parent amines are easily accessible by reduction of one or two pyridine rings of 1,10-phenanthroline.^{7c} It is anticipated that due to a spatial proximity of the two nitrogens, a substitution of one or both of them with bulky groups should lead to helical chirality of the resulting molecules. The spectroscopic investigations of helically chiral *N*-nitrosamines may lead to a better understanding of the nitrosamine chromophore.

Herein we describe the synthesis, structure, and a simple method of resolution of *N*-nitrosamines **1b** and **2b** by enclathration

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