

Bohlmann F. Zur Konfigurationsbestimmung von Chinolizidin-Derivaten.
(On the determination of configurations of quinolizidine derivatives.)
Chem. Ber. 91:2157-67, 1958.
[Organic-Chemical Institute, Technical University, Braunschweig,
Federal Republic of Germany]

Characteristic infrared (IR) frequencies are described which are only visible in the spectra of tertiary amines with a trans-diaxial orientation of the free electron pair of a nitrogen and an adjacent hydrogen. These bands allow researchers to distinguish between cis- and trans-quinolizidines, a ring system present in many alkaloids. [The *SCI*[®] indicates that this paper has been cited in over 520 publications since 1961.]

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"This paper was written while I was interested in the stereochemistry of matrine¹ and related alkaloids. While transforming matrine into derivatives it was obvious that infrared (IR) bands in the region between 2,700 and 2,800 cm^{-1} depend on the stereochemistry and conformation of the quinolizidine part. By preparing several model compounds, including deuterated ones, the origin of these IR bands could be explained. In addition to investigations of quinolizidine and of the isomeric hexahydrojulolidines, the IR spectra of several natural compounds and in part specifically deuterated derivatives also were measured. The deuterated quinolizidines especially clearly showed that corresponding IR bands also were present for C-D valence vibrations. Furthermore, the limitation of the occurrence of these bands was tested. As expected, the so-called 'trans bands' disappeared in the corresponding enamines,

N-oxides, or ammonium salts. The special nature of the hydrogens oriented trans-diaxial to the free electron pair of a nitrogen was visible also in the enhanced reactivity in some reactions of quinolizidine derivatives if compared with the reactivity of the corresponding cis-hydrogens.

"After moving to the Technical University of Berlin, together with D. Schumann, I demonstrated that the characteristic differences of these types of hydrogens also could be shown by ¹H and ²H NMR spectroscopy.² While in tertiary amines, IR spectra allow the assignment of trans-diaxial oriented α -hydrogens. The chemical shifts of the corresponding cis-hydrogens are characteristic in the ¹H NMR spectra; thus both methods are complementary.

"Our investigations in the first years at Berlin then dealt with the structure elucidation of further lupine alkaloids. Again the characteristic IR bands were important to elucidate the stereochemistry of several alkaloids. Furthermore, conformations in solution could be studied, for example, in the sparteine series.

"Why has this paper been frequently cited? The described empirical rule in the IR spectroscopy of tertiary amines was extremely useful, as the number of alkaloids which are derivatives of quinolizidine or of related compounds has been raised dramatically in the last 20 years. An extremely large group is the indol alkaloids, which are mostly derived from quinolizidine. However, also in other tertiary amines with α -hydrogens, the presence or absence of these IR bands are of high diagnostic value."³

1. Bohlmann F, Weise W, Rahtz D & Arndt C. Die Konfiguration des Matrins. *Chem. Ber.* 91:2176-89, 1958.
2. Bohlmann F & Schumann D. Über die NMR-Spektren von Lactamen. *Tetrahedron Lett.* (28):2435-40, 1965.
3. Gofeblewski W M & Wróbel J T. The lythraceae alkaloids. (Manske R H F & Rodrigo R G A, eds.) *The alkaloids: chemistry and physiology.* New York: Academic Press, 1981. Vol. 18. p. 263-322.