Nitrogen-15 Magnetic Resonance Spectroscopy. Configuration of *N*-Nitrosamines

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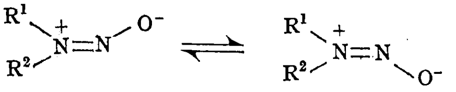
π-BONDING between the adjacent nitrogen atoms in *N*-nitrosamines leads to restricted rotation about the N–N bond and the existence of the configurational isomers (I) and (II).[1] The characteristic temperature-dependent coalescence sequence exhibited by the n.m.r. spectra of these compounds confirms the existence of an equilibrium between (I) and (II). In certain instances it has proved possible to separate these configurational isomers.[2]



(I) (II)

The early configurational assignments[1] have been reversed on the assumption that as one alkyl group in a series of compounds becomes larger it tends to exist *trans* to the nitroso-oxygen atom.[3,4] From their investigation of isomer ratios and solvent effects in unsymmetrical nitrosamines, Karabatsos and Taller[4] have concluded that the resonances due to α-methyl and α-methylene protons occur at higher magnetic fields when *cis* to the nitroso-oxygen atom rather than *trans*, while the reverse is true for α-methine protons.

A series of [*nitroso*-^{15}N]-*N*-nitrosamines having an ^{15}N-enrichment of 99% have been investigated in these laboratories. The nitrogen-15 isotope has a nuclear spin = ½ and the absence of an electric quadrupole moment readily allows the detection of its coupling with neighbouring protons. Characteristically, geminal ^{15}N–C–H and vicinal ^{15}N–C–C–H couplings through sp^3-hybridized carbon atoms are small with values[5] falling in the range 0·6—1·4 c./sec. In formamidines[6] and formamides,[7] where the geminal ^{15}N–C–H coupling involves an sp^2-hybridized carbon, the values of the coupling constants are substantially increased. Kintzinger and Lehn[8] have called attention to the strong dependence of the ^{15}N=C–H coupling on the orientation of the nitrogen lone-pair in oximes. In addition, the pH-dependence of the nitrogen-15 coupling with the ring protons in [^{15}N]quinoline has been observed.[9]

We report a configurational dependence of the

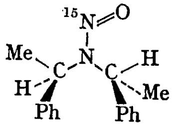
Chemical shifts and cis- *and* trans-^{15}N–N–C–H *coupling constants in* [nitroso-^{15}N]-*N-nitrosamines*

	Coupling constants[a,b]		Chemical shifts[c]	
R^1 ,R^2	J_{cis}	J_{trans}	*cis*	*trans*
$PhCH_2$	0·5	2·1	4·83	5·32
Me	0·8	2·2	2·95	3·69
$PhCH_2$	0	2·4	4·85	5·29
CH_2Me	0·8	2·5	3·56	4·13
$PhCH_2$[d]	0	3·1	4·77	5·25
$CHMe_2$	0	2·4	4·92	4·58
$PhCH_2$[d,e]	0	—	4·84	—
CMe_3	—	—	—	—
$PhCH_2$	0	2·4	4·63	5·18
$PhCH_2$	0	2·4	4·63	5·18
PhCHMe[f]	0	3·0	6·28	5·00
PhCHMe	0	3·0	6·28	5·00
Ph[e]	—	—	—	—
Me	0·8	—	3·43	—

[a] All constants are expressed in c./sec. [b] The uncertainty in these values is estimated to be ± 0·2 c./sec. because of broadening, and in some cases, partial overlap of peaks. [c] Measured in deuteriochloroform solution in p.p.m. from internal tetramethylsilane using a Varian A60 spectrometer. [d] Determined on a HA 100 spectrometer. [e] Only one configuration is present at room temperature. [f] Refers to the (±)-isomer prepared by method of C. G. Overberger, N. P. Marullo, and R. G. Hiskey, *J. Amer. Chem. Soc.*, 1961, **38**, 1374.

^{15}N–N–C–H coupling that has been observed in *N*-nitrosamines. The findings summarized in the Table indicate a marked difference in the magnitude of the ^{15}N–N–C–H coupling depending on whether the α-proton is located *cis* or *trans* to the nitroso-oxygen atom.

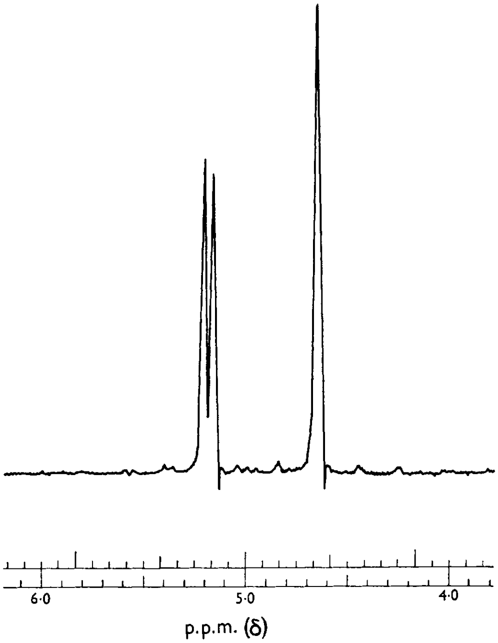
In a typical example, the n.m.r. spectrum of [*nitroso*-^{15}N]dibenzylnitrosamine shown in the Figure exhibits a high field singlet at 278 c./sec.



(III)

and a doublet (*J* 2·4 c./sec.) at 311 c./sec., measured from internal tetramethylsilane. These signals are assigned to the *cis*- and *trans*-benzyl protons respectively, using the criteria† of Karapbatsos and Taller[4] which are in agreement with predictions based on the anisotropic effects of the nitrosamino-group.[10] Compared to the spectrum of the unlabelled compound the singlet at 278 c./sec. is noticeably broadened indicating that slight coupling to the α-proton in the *cis*-configuration does occur. However benzyl t-butyl nitrosamine, which exists in only one configuration, presumably the more stable one having the benzyl group *cis* to the nitroso-oxygen atom, fails to show any measurable ^{15}N–N–C–H coupling. In none of the cases investigated does this *cis*-coupling exceed the 0·8 c./sec., observed in methyl phenyl nitrosamine. This latter compound similarly exists as only the *cis*-methyl isomer.[1,4] On the other hand, *trans* ^{15}N–N–C–H coupling in these nitrosamines falls in the range 2·1—3·1 c./sec. and this greater coupling complements the methods available of assigning configurations.

Finally, the greater deshielding experienced by the *cis*-α-methine hydrogen (than by *trans*) in $\alpha\alpha'$-dibenzyldimethylnitrosamine has been attributed to the importance of conformation (III).‡



FIGURE

In this case only the high-field quartet is coupled to nitrogen-15 which is consistent with the greater ^{15}N–N–C–H coupling to a *trans*-hydrogen.

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† In benzene solution these signals appear at 267 and 290 c./sec. respectively, in contrast with the usual situation in which the *trans* α-protons experience the greater diamagnetic shift.

‡ For a discussion of comformational assignments see ref. 4.

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