A ^{13}C Fourier Nuclear Magnetic Resonance Study of Conformational Effects in some *N*-Nitroso-compounds

By P. S. PREGOSIN and E. W. RANDALL*

(*Department of Chemistry, Queen Mary College, Mile End Road, London E.*1)

Summary The carbon-13 "Fourier" n.m.r. spectra of a series of *N*-nitrosamines and *N*-nitrosoanilines have been obtained and show that the carbon shifts in these systems are dependent on the orientation of the nitroso-oxygen atom: definitive evidence for the coplanarity of the two π-systems in *N*-methyl-*N*-nitrosoaniline is presented.

THE sensitivity of carbon chemical shifts to structural and conformational effects is well established,[1] but few studies have dealt with the effects of restricted rotation, and none with hindered rotation around a phenyl–X bond.

We report a ^{13}C Fourier n.m.r. study of some *N*-nitrosamines and *N*-nitrosoanilines which demonstrates *cis–trans* differences in shifts along the alkyl chain and definitively establishes that rotation around the N–phenyl bond in *N*-methyl-*N*-nitrosoaniline is restricted. Preliminary results are shown in the Table. ^{13}C spectra for the symmetrical dialkylnitrosamines show the magnetically inequivalent isomers consistent with ^{1}H n.m.r. studies.[2] Assignments were made using expected aliphatic substitution effects[3] and selective proton decoupling techniques.

We find that the relative positions of the aliphatic carbon resonances are consistent with known alkyl substituent effects.[3] There is no significant difference between the alkyl substituent effects in the *cis* and *trans* forms. Substitution of phenyl for methyl on nitrogen (see Table) affects only a small upfield shift in the α-carbon.

The differences in carbon chemical shifts, $\Delta\delta$, between the corresponding *cis* and *trans* isomers may be seen to vary from 5·7—10·1 p.p.m. for the α-carbons, 1·0—4·6 p.p.m. for the β-carbons, and 0·2—0·6 p.p.m. for the γ-carbons, with the *trans* isomers giving the lowest field absorptions in the α and β cases. A similar low-field shift of the methyl carbon *trans* to oxygen has been observed for *NN*-dimethylformamide.[4]

The ten-fold increase in $\Delta\delta$ for ^{13}C relative to protons cannot be accounted for solely on the basis of the magnetic anisotropy effect of the nitrosamino-group since this effect is expected to be independent of the nucleus under observation. It seems possible that an electric field effect, which is thought to be significant in amides[4] and in the case of the α-protons of nitrosamines[5] makes an appreciable contribution to the observed difference.

The presence of only one methyl carbon absorption in

N-methyl-*N*-nitrosoaniline confirms that only one isomer is present in reasonable amount (*i.e.* $>1\%$). The value for the shift of the methyl carbon supports the idea[2b] of a *cis* orientation of the methyl carbon and nitroso-oxygen groups. The aromatic region (see Figure) shows six resonances of approximately the same intensity with the exception of C-1, which is expected to be less intense due to the absence of appreciable Overhauser enhancement,[6] and its attachment to ^{14}N. This observation provides definitive evidence for the inequivalence of the *ortho* and *meta* aromatic carbons, which is explicable only in terms of restricted rotation around the phenyl–nitrogen bond. Free rotation should, as a result of the approximately planar nitrosamino-system lead to only four aromatic carbon resonances. Indeed, in the higher homologues (see Table), where interactions of the aliphatic side chains with the ring carbons are possible, only four aromatic carbon absorptions are detected. The simplest and most probable rationalisation is a coplanar arrangement of the two π-systems in *N*-methyl-*N*-nitrosoaniline, a view which is consistent with a recent electronic absorption study of these systems.[7]

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^{13}C *chemical shifts*[a] *of the aliphatic carbons of* N-*nitrosamines and* N-*nitrosoanilines*

Compound R^{1}R^{2}NNO		Chemical shifts					
		α		β		γ[b]	
R^1	R^2	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
Me	Me	32·6	40·5				
Et	Et	38·4	47·0	11·5	14·5		
Pr^n	Pr^n	45·2	54·2	20·3	22·5	11·3	11·8
Pr^i	Pr^i	45·4	51·1	19·1	23·7		
Bu^n [c]	Bu^n [c]	41·8	51·9	28·9	31·1	20·3	20·9
Bu^i	Bu^i	50·4	59·9	26·5	27·5	20·1	20·5
Ph	Me	30·9	—	—	—	—	—
Ph	Et	38·9	—	11·8	—	—	—
Ph	Pr^n	44·9	—	20·2	—	11·5	—
Ph[d]	Bu^n [d]	43·1	—	29·0	—	20·6	—
Ph	Bu^s	52·3	62·0	27·4[e]	28·9[e]	11·0	11·2
		—	—	17·7[f]	20·2[f]	—	—
Ph[g]	Bu^t [g]	—	61·8	—	30·1	—	—

[a] Chemical shifts are reported in p.p.m. downfield from internal Me$_4$Si and are thought to be accurate to ± 0·1 p.p.m. [b] Assignments may be reversed. [c] δ-Methyl groups appear at 13·8 p.p.m. as a broad singlet. [d] δ-Methyl group at 13·7 p.p.m. [e] Value shown is for methylene carbon. [f] Value shown is for methyl carbon. [g] Solution in CDCl$_3$.

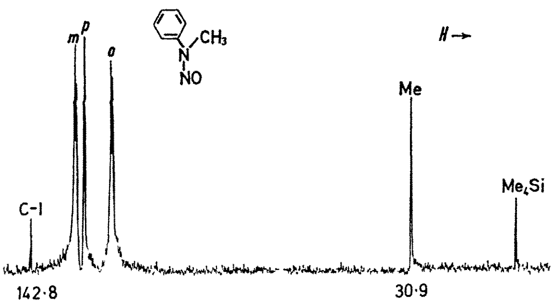

FIGURE. ^{13}C *"Fourier" power spectrum of* N-*methyl*-N-*nitrosoaniline at* 22·63 *MHz measured as a "neat" liquid containing* 10—15% C_6F_6, *used for field-frequency locking, and* 10% Me$_4$Si *as internal reference. Wide band decoupling of the protons was employed to simplify the spectrum. The spectrum is the result of* 1024 *pulses each of* 40 μs *duration spaced approximately* 0·4 s *apart.*

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