Nitrogen-14 Nuclear Magnetic Resonance Studies of Trifluoramine Oxide, Nitrogen Trifluoride, and Related Compounds

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TRIFLUORAMINE OXIDE,[1-3] ONF_3, is an unusual amine oxide, with NF_3 a non-basic amine. The NO stretching frequency, 1690 cm.$^{-1}$, resembles the 1600 cm.$^{-1}$ found in CF_3NO[4] rather than the 950—970 cm.$^{-1}$ in the amine oxides $R_3N^+–O^-$ (formed by the more basic amines). This double-bond character in ONF_3 is attributed[1] to delocalisation of lone-pair (in this case n_O) electrons into NF σ^* orbitals, as in CF_4 and chlorofluoromethanes, enhanced by the high effective electronegativity of the nitrogen.

We have measured the ^{14}N n.m.r. shifts of ONF_3, and of NF_3, NOF, NO_2F, CF_3NO, and CF_3NO_2, with wide-line (Varian 4300B) equipment, and nitromethane as external reference. Relative to saturated aqueous nitrite ion, the shifts (in brackets, line-widths at half-height) in p.p.m. are: ONF_3, +376 (208) at −120°; NF_3, +238 (225) at −130°; NOF, +128 (90) at −60° to −105°; NO_2F, +297 (52) at −65° to −155°. The spin–spin structure is not resolved. The shift for CF_3NO is −193 (140) at −90° to −130°, and for CF_3NO_2 (preliminary value) +225 (35) at −60°. The ^{19}F resonance for NO_2F is −221 p.p.m. from $CFCl_3$ at −60°.

The Figure compares the ^{14}N shift, on removal of the oxygen from nitrogen in ONF_3 to leave $:NF_3$, with corresponding shifts for related compounds. The alkylamines,[5] ammonia,[5] and ammonium ions,[5] with trimethylamine oxide[5,6] and hydroxylammonium ions,[5] clearly form a class of their own. All the other compounds have nitrogen resonances at lower field, and show systematic downfield shifts on removal of the oxygen atom, to leave NF_3, or a nitrosyl or nitroso-compound (aromatic† or aliphatic $C{\cdot}\ddot{N}{:}O$, R_2NNO[7]); nitrite ion or RONO†; N_2O_3,[7] an azine,[5] or a furazan,[6] or even nitrogen[8] (liquid, compared with N_2O[8]).

Theory[9] shows that the de-shielding mainly depends on the magnetic excitation of electronic states, involving rotation of charge, *e.g.* $n \rightarrow \pi^*$ or σ^*, σ or $\sigma^* \longleftrightarrow \pi$ or π^*, and is inversely proportional, roughly, to the energy ΔE of the most accessible of these, often $n \rightarrow \pi^*$, or $n \rightarrow \sigma^*$ if there is no π^* orbital. This ΔE varies from *ca.* 10 ev for saturated molecules, resonating at high field, to *ca.* 2 ev for the blue *C*-nitroso-compounds, at very low field.

The methylamines and ammonia have ^{14}N resonances within a small range, 10—15 p.p.m., at high field. The shift on protonation is very small and downfield, showing that the n_N electrons are not active in paramagnetic de-shielding. Addition of oxygen at the nitrogen lone pair moves the resonance downfield by nearly 100 p.p.m., due to the inductive effect on the diamagnetic shielding, to $\sigma \rightarrow \sigma^*$ transitions between CN and NO bonds, and to $n_O \rightarrow \pi^*$ states. In all other cases, the removal of oxygen from nitrogen to leave a lone pair, like the de-protonation of azines,[5,10] allows de-shielding by $n_N \rightarrow \pi^*$ or σ^* excitation (*cf.* pyridine, the *N*-oxide, and *N*-hydroxonium ion[5]).

The XNO_2 compounds, with no n_N electrons, have rather similar shifts (Figure), showing a similar effect at nitrogen of the $\sigma \rightarrow \pi^*$ transitions. In contrast the $X{\cdot}\ddot{N}{:}O$ line

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† Measured by L.-O. Andersson, Varian Research Laboratory, Zürich.

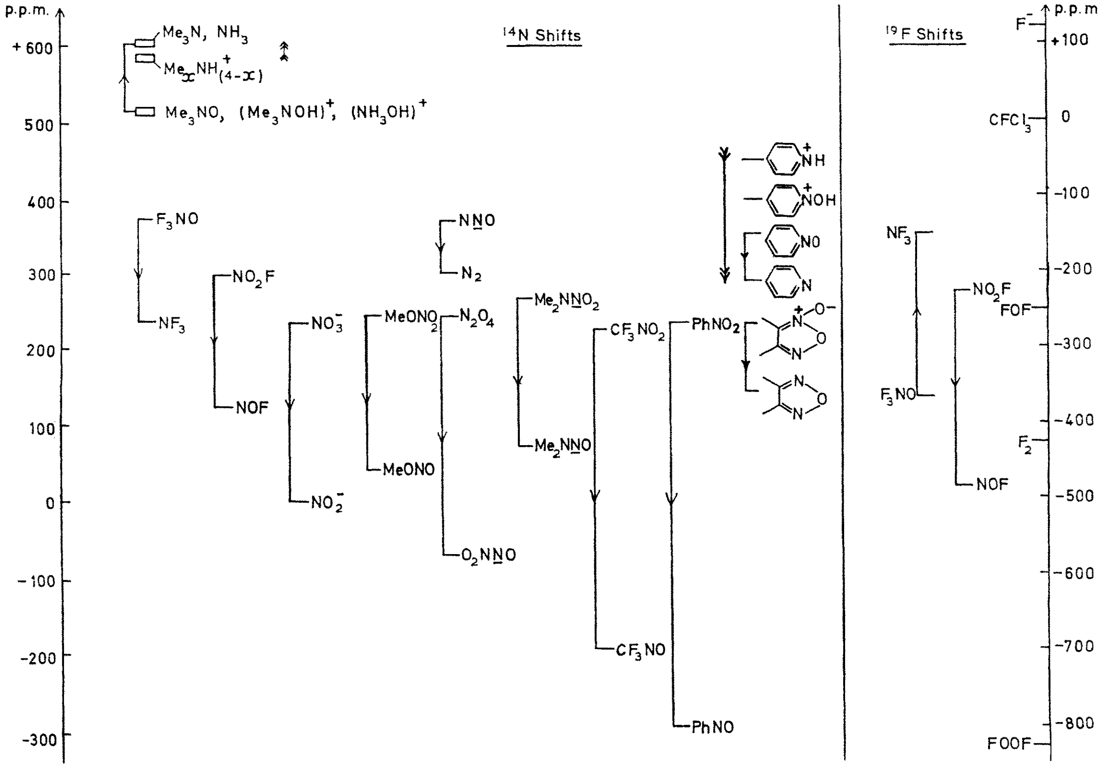

FIGURE. *S shifts on removal of O from N*: (——→——) *and on deprotonation*: (≫—≫).

moves upfield as the $n_N \rightarrow \pi^*$ band shifts to higher frequency with increasing inductive stabilisation of the lone pair, in the order C·NO < $O_2N\mathit{N}O$ < NO_2^- < NOF <NF_3; and in RONO, $R_2N\mathit{N}O$, and NOF, also with raising of the π^* orbital by inflow of n_X electrons.

In NF_3, $n \rightarrow \sigma^*$ excitation can explain the de-shielding relative to NH_3 and the amines (although the u.v. spectrum of NF_3 is rather featureless)[11]. The NF σ^* orbitals must be quite low in energy as the bond is rather weak; $D(F–NF_2)$ is 57 kcal.mole.$^{-1}$, the radical NF_2 being rather stable.

The upfield shift of ONF_3 relative to the XNO_2 compounds probably reflects a smaller $\sigma \rightarrow \pi^*$ separation in XNO_2 as compared with the $\sigma_{NO} \rightarrow \sigma_{NF}^*$ separation in ONF_3; the latter is increased if n_O electrons move into σ^* orbitals. But the N–F bond in ONF_3 is weaker than in NF_3,[3] and breaks before the N–O bond, in the mass spectrometer and in chemical reactions.[1] The pattern of the shifts illustrates the difference between the N–O bond in ONF_3 and a true double bond, as in the C·N : O compounds.

In ^{19}F resonance, transitions of n_F (π-type) electrons are now the most important.[9] NOF is downfield from NO_2F, but NF_3 is upfield from ONF_3. The downfield shifts correlate, at lower fields, with the weakness of the bond to fluorine, *i.e.* with a lowering of the σ^* orbitals, and perhaps with de-stabilisation of the n_F electrons. FO·OF has a very long O–F bond[12] and a very low-field ^{19}F line,[13] and is coloured (also at $-196°$).[14]

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