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NITROGEN-15 NMR COMPARISONS OF (ALKYL AND PERFLUOROALKYL) *C*-NITROSO COMPOUNDS, AND BENT AND LINEAR NITROSYL LIGANDS IN TRANSITION METAL COMPLEXES *

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Summary

The correlation of the low nitrogen shielding in alkylnitroso compounds with low-energy $n(\mathrm{N}) \rightarrow \pi^*$ circulations is supported by the observation of perfluoro effects: the nitrogen shielding increases (by ca. 140 ppm) when alkyl groups on the α-carbon are replaced by fluorine or by perfluoroalkyl groups, as the electronegative substituents stabilize the n(N) relative to the π^* (NO) orbital. Analogy is drawn between the *C*-nitroso group and the strongly-bent nitrosyl ligand in transition metal complexes. For MNO angles near 120° the nitrogen is strongly deshielded, relative to linear MNO, e.g. by ca. 360 ppm for complexes of ruthenium and rhodium, and over 700 ppm for cobalt complexes. Intermediate nitrogen shifts are observed for intermediate bond angles, as in dinitrosyl complexes in which MNO deviates from linearity by up to 25°.

The NO group has a varied chemistry: NO is stable as an odd-electron molecule, as the cation NO^+, and as the dimer ONNO at low temperatures or under pressure. As a radical trap, NO combines with organic or inorganic radicals to form the bent nitroso (nitrosyl) group. With transition metals, however, NO most often coordinates as a three-electron ligand (NO^+) to give linear nitrosyls MNO; but it can act as a

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983. J.M. was one of the first group of Cambridge graduate students to work with Harry Emeléus, from October 1946.

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one-electron ligand (described as NO^-) to give MNO angles near 120°, and angles from 120° to 180° are possible with appropriate coligands [1,2]. Unexpectedly, NO can also chelate through oxygen, effectively in hyponitrito form $^-ONNO^-$ [3]. Nitrogen NMR spectroscopy is a peculiarly sensitive probe of structure of the nitrosyl group [4], as we shall show.

The work to be described hinges on the preparation of CF_3I by Victor Kerrigan in 1947 (while in Cambridge on secondment from I.C.I.) [5]. Emeléus was keen to get perfluoroalkyl chemistry going, and had Douglas Payne working with CF_3Cl and Arthur (Ash) Banks with CF_3Br, which he made by fluorinating CBr_4 with BrF_3. The unsuccessful attempt by Simons and co-workers [6] to make CF_3I by fluorinating CI_4 with IF_5 had used copper apparatus and ended up with C_2F_6. Using silica (or even Pyrex) traps, Kerrigan made CF_3I from these reagents in good yield. CF_3I boils at $-22.5°C$. With Emeléus's experience of fluorine chemistry and vacuum techniques, the foundation was laid for the Cambridge work on perfluoroalkyl derivatives.

Our early attempts at either homolytic or heterolytic exchange of iodide for other functional groups led all too often to fluoroform, CF_3H; the most fruitful procedure at that time turned out to be photolytic [7]. The UV spectrum of CF_3I resembled that of alkyl iodides. It was recorded on photographic plates with varying exposures, and the spectrum of a (very noisy) iron are recorded also. Optical densities were matched by eye and wavelengths measured by reference to the iron arc spectrum, with a hair inserted as marker in the comparator. At Emeléus's suggestion the early photochemical work was done in Ken Ivin's apparatus for measuring quantum yields, in Dainton's lab. Irradiation with the mercury 254 nm line gave CF_3 radicals. Addition of mercury to prevent primary recombination gave compounds such as CF_3HgI, the initiation of polymerisation of ethylene, and with NO, the blue gas CF_3NO. At that time, products were "identified" by their molecular weight (measured by Regnault's method) and elemental analysis. The first IR spectroscopic work on CF_3NO was done with Harry Poole's (single beam, optical bench!) equipment at University College London in the early 1950s [8]. Delia Agar was spectroscopic advisor on this IR as well as the earlier UV work.

CF_3NO was discovered by Ruff and Giese in 1936 as a product of fluorination of AgCN containing $AgNO_3$ and Ag_2O impurities, but they could not separate it from a colourless compound thought to be $FCONF_2$ [9]. The preparation of CF_3NO and other R_FNO by use of NO to trap the perfluoroalkyl radical [10] was suggested by Hinselwood's use of NO to inhibit radical chain reactions [11]. Alkylnitroso compounds RNO dimerise to azodioxides $RN(O){=}N(O)R$ or isomerise to aldoximes ($RCH_2NO \rightarrow RCH{=}NOH$), but Hammick had shown that the nitroso group could be stabilised in monomeric from by electronegative α-substituents such as halogens [12].

The link between CF_3NO and nitrogen NMR spectroscopy was N_2O_3, which is stable as a blue liquid or solid at low temperatures. As the electronic spectrum of CF_3NO was being measured at low temperatures [13], at University College in the early 1950s, it was convenient to measure N_2O_3 solutions in this way [14] as an aid to the estimation of this compound in Bunton and Stedman's nitrosation work [15]. The constitution of N_2O_3 was not then known: Sidgwick gave a nitrito structure ONONO [16], but the Ingolds favoured a nitronitroso structure O_2NNO [17]. There was still no firm evidence in 1967 as the solid is disordered [18], and the microwave

TABLE 1

^{15}N NMR SHIFTS IN *C*-NITROSO COMPOUNDS

Compound[a]	$\delta(^{15}N)$ (ppm)[b]
$CF_3CF_2CF_2C(CF_3)_2NO$ in $CFCl_3/CCl_4$	427.6
$CF_3(CF_2Cl)CFNO$ in $CHCl_3$	461.3
$(CF_3)_2CFNO$(liq)	458.9
$CF_3CF_2CF_2NO$ in $CFCl_2CF_2Cl$	485.8
Me_3CNO in $CHCl_3$	593.8
1,4-$C_6H_4(COOCMe_2CMe_2NO)_2$[c] in $CHCl_3$	603.0

[a] Measured at 25°C, in natural abundance of ^{15}N. [b] Relative to liquid CH_3NO_2, downfield positive. [c] We thank Dr. T.R. Sharpe for this compound.

spectrum has not yet been reported [19]. By then, however, ^{14}N NMR spectroscopy was a possibility, and contact was made (via Jim Feeney) with Varian's wideline NMR man in Zurich, Lars Andersson. N_2O_3 gave two ^{14}N lines, a nitroso line with δ 297 ppm and a nitro line with δ 65 ppm [20]. This work was followed up with Bill van Bronswijk at University College London, using Nyholm's wideline spectrometer, by ^{14}N studies of nitroso (nitrosyl) [21] and nitro [22] compounds, including CF_3NO and CF_3NO_2. In the XNO series, with X = F, Cl, Br, Me_2N, MeO, RS, CF_3S, CF_3, Ph, etc. there was a clear trend of decrease in nitrogen shielding as the $n(N) \rightarrow \pi^*$ band moves to longer wavelengths, i.e. with decreasing energy of the $p(n) \rightarrow p\pi^*$ circulation which reinforces the magnetic field. Thus the blue colour of nitroso compounds correlates with low-field nitrogen lines. The π^*(NO) LUMO is low-lying because of the high electronegativity of nitrogen and oxygen, and the n(N) (lone pair) HOMO is high-lying in alkylnitroso compounds.

^{14}N work in the 1960s on transition metal complexes showed that linear nitrosyls resonate at medium field [23,24]. The *C*-nitroso analogy suggested that nitrogen should be much less shielded in bent nitrosyls. The search for low-field resonances took several years, because of the low sensitivity of ^{14}N and ^{15}N NMR spectroscopy [4], the broad lines given by ^{14}N carrying a lone pair, the low abundance of ^{15}N, and the lability of the compounds.

During the 1970s high resolution work in natural abundance of ^{15}N became possible by the use of a widebore superconducting (180 MHz) spectrometer, and a range of perfluoro nitroso and related compounds has been measured in collaboration with Eric Banks at UMIST. The nitrogen shifts in Table 1 show an interesting perfluoro effect, an increase in nitrogen shielding (by ca. 140 ppm) when fluorine or perfluoroalkyl replace alkyl substituents on the α-carbon. This increase follows the stabilisation of the n(N) HOMO relative to the π^* LUMO with increase in electronegativity of the group σ-bonded to the nitrogen. It is related to the perfluoro effects used by Robin [25] to distinguish σ- and π-type orbitals in photoelectron and electronic spectroscopy, and to those observed in the ^{15}N NMR shifts of azides and azabenzenes [26].

Interestingly, although a fluorine substituent on the α-carbon would be expected to have a greater σ-inductive effect than a perfluoroalkyl group, the nitrogen

TABLE 2

NITROGEN NMR AND IR SPECTROSCOPIC MEASUREMENTS OF TRANSITION METAL NITROSYLS WITH DIFFERENT GEOMETRIES

Compound	Solvent	n [a]	δ(NO) [b] (ppm)	Coordination geometry	$\nu(^{14}NO)$ [c] (cm^{-1})	Angle MNO [d] (deg)	Angle NMN [d] (deg)
Mononitrosyls, linear							
$[Os(NH_3)_5(NO)]Cl_3$	H_2O	6	−75 [e] −72 [f]	oct.			
trans-$[RuCl_3(^{15}NO)(PPh_3)_2]$	CH_2Cl_2	6	−36.7	oct.	1876	180	–
$[Co(CO)_3(NO)]$ [g]	Benzene	10	14	tetr.	1805	180	–
$W[(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ [h]	$CHCl_3$	6	16.5	piano-stool	1655		
trans-$[RhCl(^{15}NO)(PPr^i_3)_2](ClO_4)$ [i]	$CHCl_3$	8	24.0	sq. pl.	1842		
$Mo[(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ [h]	$CHCl_3$	6	37.6	piano-stool	1663		
Dinitrosyls							
$[Os(^{15}NO)_2(PPh_3)_2]$	Benzene	10	10.6 [j]	tetr.	1665,1605	174,179	139
$[Ru(^{15}NO)_2(PPh_3)_2]$	Benzene	10	50.7	tetr.	1665,1615	171,178 or 168,175	139 140
$[CoCl(NO)_2(PPh_3)]$ [k]	Acetone	10	62	tetr.	1829,1770		
$[Rh(NO)(^{15}NO)(PPh_3)_2](ClO_4)$	CH_2Cl_2	10	81.4 [l]	tetr.	1759,1714	159	157.5
$[W(\eta^5\text{-}C_5H_5)Cl(NO)_2]$ [h]	$CHCl_3$	6	172.9	piano-stool	1733,1650		
$[Mo(\eta^5\text{-}C_5H_5)Cl(NO)_2]$ [h]	$CHCl_3$	6	185.4	piano-stool	1759,1665		
Mononitrosyls, strongly-bent							
trans-$[RuCl(CO)(^{15}NO)(PPh_3)_2]$	Benzene	8	342.3	sq. py.			
trans-$[RhCl(CO)(^{15}NO)(PPr^i_3)_2](ClO_4)$ [i]	CH_2Cl_2	8	368.2	sq. py.	1712		
$[Co(^{15}NO)(salen)]$ [i]	Me_2SO	8	736.9	sq. py.	1624	127	

[a] In $\{M(NO)_m\}^n$, where n is the total of d(M) and π^*(NO) electrons [1]. [b] Relative to liquid CH_3NO_2, downfield positive, measured at 25°C. [c] Nujol mull (except for values from ref. 27 measured in CH_2Cl_2); cf. 1595 cm^{-1} for CF_3NO gas [8]. [d] Refs. 1, 31, 32. [e] Ref. 29 (^{14}N). [f] Unpublished work with Frank Bottomley (^{14}N). [g] Ref. 23 (^{14}N). [h] Ref. 27. [i] Ref. 28, $J(Rh^{15}N)$ 52 Hz. [j] $J(P^{15}N)$ 6.2 Hz. [k] Ref. 24 (^{14}N). [l] $J(Rh^{15}N)$ 40.9 Hz.

shielding also decreases in the sequence $(R_F)_3CNO > (R_F)_2CFNO > R_FCF_2NO$, by about 30 ppm per geminal fluorine (Table 1). This could be explained in terms of destabilising interaction of the non-bonding electrons on nitrogen with those on the geminal fluorine.

In 1979 ^{15}N shifts were reported by Legzdins, Roberts, and co-workers [27] for (linear) mono- and di-nitrosyl piano-stool complexes of Cr, Mo, and W, measured in natural abundance of ^{15}N on a widebore 180 MHz spectrometer. Our attempts to measure bent nitrosyls were unsuccessful, and enrichment was needed. The first unequivocal low-field ^{15}N lines for transition metal nitrosyl complexes were observed with 99% ^{15}N-enrichment, on the 400 MHz spectrometer at Warwick [28]. The ^{15}N shifts of bent apical nitrosyl ligands (with MNO angle ca. 120°) in square-pyramidal complexes of Rh or Co were compared with those of linear mono-nitrosyls in square-planar or tetrahedral complexes of the same metals with similar coligands. The ^{15}N deshielding for the bent compared with the linear ligand was 350–450 ppm in the rhodium complexes, and a similar figure has now been observed for ruthenium (see Table 2); it was over 700 ppm for the cobalt complexes.

The ^{15}N shift is thus a useful criterion of the MNO geometry in solution, which cannot necessarily be inferred from that in the solid, such is the lability of the nitrosyl group. We are currently studying complexes in which the coordination geometry and MNO angle are different in the crystal and in solution. The $\nu(NO)$ stretching frequency is by no means characteristic of the MNO angle, as Table 2 illustrates.

Interestingly, the ^{14}N or ^{15}N shifts of linear mononitrosyls so far measured (of Cr, Fe, Co, Mo, Ru, Rh, W, and Os) [23,24,27–29] appear to vary periodically, as observed for ^{13}C shifts in transition metal carbonyls [30], though with some dependence also on the coordination geometry and on the coligands. The shielding tends to increase across the series of the transition metal, and increase also down the group.

The question then arises, as to whether nitrosyls with MNO angles between 120 and 180° have intermediate nitrogen shifts. We have therefore measured dinitrosyls of Rh, Ru, and Os with distorted tetrahedral geometry, since the nitrosyls interact so as to open out the MNN angle, and bend slightly [31]. Table 2 shows that the dinitrosyl line for a given metal is somewhat downfield of the line at medium field for the mononitrosyl. The deshielding seems to decrease across the series, from ca. 150 ppm for Mo or W, to ca. 85 ppm for Ru or Os, and to ca. 53 ppm for Co or Rh (but this variation may include some effects of changes in coordination geometry, and of coligands). In the $\{M(NO)_2\}^{10}$ series of quasi-tetrahedral complexes with two PPh_3 coligands the NMN angle opens out and the OMO angle opens further (the oxygens bend apart) increasingly across the transition metal series (from Fe to Co, Ru to Rh, and Os to Ir), and also from the first to the second or third series [1,31–33]. Since the nitrogen shielding increases with increase in the HOMO-LUMO gap (for the circulation of charge) at nitrogen, our results agree with the suggestions [1,2,32,33] that the distortions help to stabilize $d\pi$ electrons by delocalization into the low-lying $\pi^*(NO)$ orbital, which is thereby destabilized. (There is also some destabilization of the nitrogen's coordinating electron pair as this becomes less σ-bonding, in avoiding the $d\sigma^*$ electrons.)

As to the $[Pt(ONNO)(PPh_3)_2]$ complex, in which NO unexpectedly coordinates in dimeric form through oxygen to form a five-membered ring, the nitrogen shift

(34.9 ppm) shows the relationship to hyponitrite ion (with δ 83 ppm in aqueous solution), since coordination shifts are usually fairly small.

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