Oxygen-17 Nuclear Magnetic Resonance. Part I. Oxygen–Nitrogen Groupings

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Oxygen-17 shifts are reported for N_2O_3, N_2O_4, MeONO, Me_2NNO, NO_2^+, and NOCl, with ^{17}O in natural abundance. These are compared with literature values of ^{17}O shifts in other oxygen–nitrogen groupings, and with the corresponding nitrogen shifts. The shifts of adjacent oxygen and nitrogen in the same chromophore are roughly in the proportion of their respective values of $\langle r^{-3}\rangle$, which gives the dependence of the paramagnetic shielding term (σ_p) on the radius of the 2*p* orbitals. The oxygen resonances tend to move downfield as the lowest-energy electronic absorption moves to longer wavelengths, but the scatter is large. The oxygen shielding in XNO and XNO_2 compounds (as in RCOX) reflects the conjugative effect of the substituent X. This contrasts with the nitrogen shielding, in which inductive effects are relatively more important. Inductive effects may however be among those responsible for oxygen shift relationships, in certain sets of compounds, that differ from the overall trends. The relative importance of the orbital terms that contribute to σ_p is compared for oxygen and nitrogen in these groupings.

WE report the ^{17}O chemical shifts of some oxygen–nitrogen compounds, measured with ^{17}O in natural abundance (0·037%) and with wide-line equipment because of the quadrupolar broadening (^{17}O has $I = 5/2$). The shifts are given in the Table relative to $H_2{}^{17}O$, together with literature values for some related compounds. The samples were measured neat and at room temperature unless a solvent or a temperature is given. Since the reference substances $H_2{}^{17}O$ and $^{14}NH_4$(aq.) resonate at high field, the shifts are all to low field and are recorded as positive.

EXPERIMENTAL

The measurements were made (by L.-O. A. in 1968) with a Varian WL-9 spectrometer at 8 MHz. Large modulation amplitudes were used in order to increase the intensity of the weak signals. In many cases the dispersion signal was studied. Each shift value is the average of several measurements, with H_2O as external reference.

DISCUSSION

The Relation between the Nitrogen and Oxygen Shifts.—The ^{14}N shifts of nitroso-[1] and nitro-[2] and related groups are given also in the Table. This and Figure 1 show that there is a rough proportionality between the shifts of adjacent nitrogen and oxygen in the same chromophore. The line in Figure 1 superimposed on the plotted points, which fits them reasonably well, has slope 1·75, which is the ratio of $\langle r^{-3}\rangle_{\text{oxygen}}$ to $\langle r^{-3}\rangle_{\text{nitrogen}}$, where $\langle r^{-3}\rangle$ is the mean inverse cube of the 2*p* electron radius (as given by Barnes and Smith [3]). The inverse cube is the form of the radial dependence of the paramagnetic shielding constant, as in Pople's approximate expression [4] for the local term,

$$\sigma_p{}^{A} = \frac{-e^2\hbar^2\langle r^{-3}\rangle}{2m^2c^2(\Delta E)}\left[Q_{AA} + \sum_{B \neq A} (Q_{AB})\right]$$

which refers to the atom A bound to other atoms B.

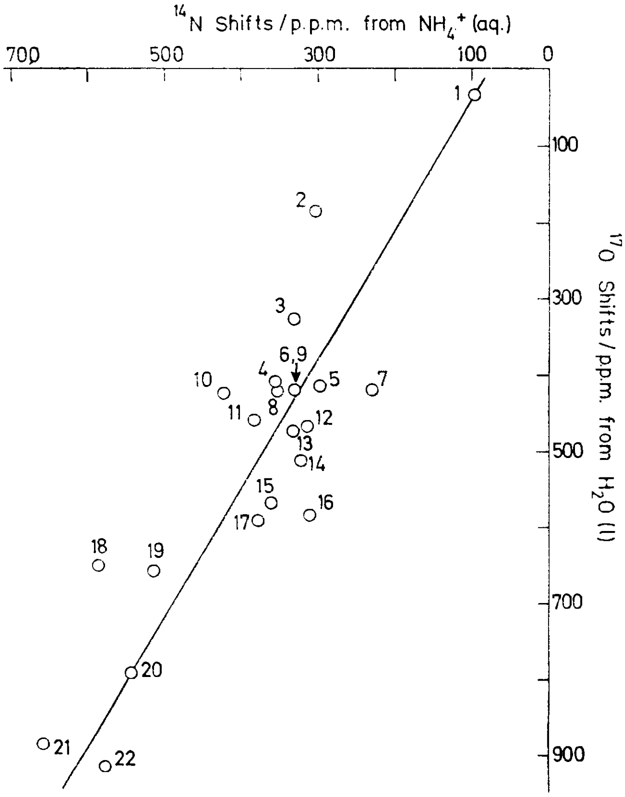

FIGURE 1 Correlation of the oxygen and nitrogen shifts; the numbers refer to the Table; the line is of slope 1·75

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[1] L.-O. Andersson, J. (Banus) Mason, and W. van Bronswijk, *J. Chem. Soc.* (*A*), 1970, 296.

[2] J. Mason and W. van Bronswijk, *J. Chem. Soc.* (*A*), 1970, 1763, and references therein.

[3] R. G. Barnes and W. V. Smith, *Phys. Rev.*, 1954, **93**, 95.

[4] J. A. Pople, *Discuss. Faraday Soc.*, 1962, **34**, 7; *J. Chem. Phys.*, 1962, **37**, 53, 60; 1963, **38**, 1276; *Mol. Phys.*, 1963, **7**, 301.

The Q's are constitutive terms, and ΔE is a mean or effective excitation energy.

Similarly, if the ^{17}O shifts[5] are plotted against the shifts of adjacent ^{13}C in alcohols, ethers, and carbonyl compounds of various types, the points group themselves around a line of slope 3·5, which is the ratio of $\langle r^{-3}\rangle_{\text{oxygen}}$ to $\langle r^{-3}\rangle_{\text{carbon}}$.

The scatter in the nitrogen : oxygen and carbon : oxygen correlations is reduced somewhat if certain corrections are made. First, solvent shifts are large in oxygen resonance (particularly in aqueous solutions, and where ions are involved). They are smaller in nitrogen resonance, and smaller still in carbon resonance. For example, the ^{17}O line of dilute aqueous acetone is 57 p.p.m. upfield, and the ^{13}C line 11 p.p.m. downfield, of the corresponding lines for pure acetone.[6] Secondly, the (nearest-neighbour) diamagnetic term[7] is about 35 p.p.m. larger for oxygen with two second-row ligands, as in $MeONH_2$, or ethers, than for oxygen with only one of these, as in RCOX, XNO, or XNO_2. Correction for this diamagnetic term thus moves the points for oxygen in the first category about 35 p.p.m. upfield relative to the rest. This correction becomes increasingly important from oxygen to nitrogen,[7] and to carbon,[8] as the possible number of such ligands increases. But even when such corrections are made, the shifts do show local trends, within closely related groups of compounds, that differ from the overall relationship.

		^{17}O		^{14}N		Long-wavelength band maxima †				
						$n \rightarrow \pi^*$/Bands		Other bands		
No.	Compound	Shift (p.p.m.)	Ref.	Shift (p.p.m.)	Ref.	λ/nm	ε	λ/nm	ε	Ref.
1	$MeONH_3^+(Cl^-$, aq.)	35	5	98	*d*			*ca.* 200		
2	$CH_2NO_2^-$ Na^+(MeOH)	190 ± 20	*a*	303	*a*			232	7940	*i*
3	$MeN\mathit{NO}_2^-$ Na^+ (aq.)	335 ± 15	*b*	327	*b*					
4	NO_3^- (aq.)	410 ± 15		353		302	7			*j*
5	HNO_3 (100%)	414	9	298	*f*	257	10			*k*
6	$CH(NO_2)_2^-$ Na^+ (aq.)	420	*a*	333	*a*			362		*i*
7	$NO_2^+HSO_4^-$(conc. H_2SO_4)	420 ± 40		228	*f*					
8	N_2O_4 (−26 °C)	420 ± 30		342	2	340	175			*l*
9	$MeNH\mathit{NO}_2$	420	*b*	330	*g*			231	7590	*m*
10	$ON\mathit{NO}_2$ (−63 °C)	425 ± 20		420	1	645	10			*n, o*
11	Dimethylfurazan	460	5	382	*h*			220	3630	*p*
12	$EtONO_2$ —O—	340								
	NO_2	470	*c*	316	*e*	265	16sh			*q, m*
13	Dimethylfurazan *N*-oxide	350								
		475	5	333	*h*			262	6760	*r*
14	$C(NO_2)_3^-$ Na^+(aq.)	514	*a*	322	*a*	415	sh			*i*
15	$PhNO_2$	569	5	345	*g*	330	165			*s*
16	$C(NO_2)_4$	590	*a*	307	*g*	272	145			*i*
17	$MeNO_2$	590	5	353	2	275	8			*t*
18	NO_2^- (aq.)	650 ± 20		585	2	280	8			*u*
						357	23			
19	$Me_2N\mathit{NO}$	660 ± 25		510	1	361	125			*v*
20	MeONO —O—	420 ± 30								
	NO	790 ± 30		541	1	341	100			*n*
21	$O_2N\mathit{NO}$ (−63 °C)	885 ± 40		655	1	645	10			
22	NOCl	915 ± 40		575	1	(335	32)			
						440	5			*w*
						475	5			
						(602	1)			

† sh = Shoulder.

[a] E. T. Lippmaa, M. Ya. Myagi, Ya. O. Past, S. A. Shevelev, V. I. Erashko, and A. A. Fainzil'berg, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1971, **5**, 1006. [b] M. Ya. Myagi, E. T. Lippmaa, S. A. Shevelev, V. I. Erashko, and A. A. Fainzil'berg, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, **6**, 1450. [c] H. E. Weaver, B. M. Tolbert, and R. C. LaForce, *J. Chem. Phys.*, 1955, **23**, 1956. [d] Measured by J. G. Vinter. [e] M. Witanowski, *J. Amer. Chem. Soc.*, 1968, **90**, 5683. [f] R. A. Ogg and J. D. Ray, *J. Chem. Phys.*, 1956, **25**, 1285. [g] M. Witanowski, T. Urbanski, and L. Stefaniak, *J. Amer. Chem. Soc.*, 1964, **86**, 2569. [h] G. Englert, *Ber. Bunsengesellschaft Phys. Chem.*, 1961, **65**, 854. [i] G. Kortüm, *Z. phys. Chem.*, 1939, *B*, **43**, 271. [j] D. Meyerstein and A. Treinin, *Trans. Faraday Soc.*, 1961, **57**, 2104. [k] R. N. Jones, G. D. Thorn, M. Lyne, and E. G. Taylor, *Nature*, 1947, **159**, 163. [l] T. C. Hall and F. E. Blacet, *J. Chem. Phys.*, 1952, **20**, 1745. [m] M. Kortüm and B. Finckh, *Z. phys. Chem.*, 1940, *B*, **48**, 32. [n] J. Mason, unpublished work. [o] J. Mason, *J. Chem. Soc.*, 1959, 1288. [p] N. Kokura, T. Rada, and K. Yokohama, *Bull. Chem. Soc. Japan*, 1961, **34**, 270. [q] R. N. Jones and G. D. Thorn, *Canad. J. Res.*, 1949, *B*, **27**, 828. [r] J. H. Boyer, V. Toggweiler, and G. A. Stoner, *J. Amer. Chem. Soc.*, 1957, **79**, 1748. [s] J. N. Murrell, 'Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963, pp. 186—187. [t] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, 1954, **58**, 1006. [u] D. L. Friedman, *J. Chem. Phys.*, 1953, **21**, 319. [v] R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 1954, 691. [w] C. F. Goodeve and S. Katz, *Proc. Roy. Soc.*, 1939, *A*, **172**, 432; E. V. Genkina, A. I. Finkel'shtein, and A. A. Artem'ev, *Doklady Akad. Nauk S.S.S.R.*, 1956, **109**, 528.

These corrections apply also to Figure 2, which shows that the oxygen line tends to move downfield as the lowest-energy electronic absorption moves to longer wavelength [*i.e.* as $(\Delta E)^{-1}$ increases], as has been demonstrated for carbonyl compounds,[9] and also for nitrogen resonance.[1,2]

XNO Compounds.—In XNO compounds the sequence of the nitrogen lines is found[1] to reflect the factors

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[5] H. A. Christ, P. Diehl, H.-R. Schneider, and H. Dahn, *Helv. Chim. Acta*, 1961, **44**, 685; H. A. Christ and P. Diehl, *Helv. Phys. Acta*, 1963, **63**, 170.

[6] W. H. de Jeu, *Mol. Phys.*, 1970, **18**, 31.

[7] R. Grinter and J. Mason, *J. Chem. Soc.* (*A*), 1970, 2196.

[8] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038.

[9] B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. Roy. Soc.* (*A*), 1962, **269**, 469.

influencing the energy of the long-wavelength $n \longrightarrow \pi^*$ transition, namely the inductive and mesomeric effects of X. As X becomes less electronegative the lone pair electrons are destabilised relative to the π^* orbital, the electronic absorption moves to longer wavelengths and the nitrogen line tends to move downfield. The observed sequence is roughly that of the inductive effect, which decreases in the order (NOF >) MeONO > $\mathrm{O_2N}N\mathrm{O}$ > $\mathrm{Me_2N}N\mathrm{O}$ > NOCl (> NOBr > RSNO > RNO). The appearance of the $\mathrm{Me_2N}N\mathrm{O}$ line at higher field than that of MeONO is attributable to the mesomeric effect, the delocalisation of lone-pair electrons on X into the (NO) π^* orbital, raising the excitation energy, so that the line tends to shift upfield by an amount that decreases in the order $\mathrm{Me_2N}N\mathrm{O}$ > MeONO > NOCl > RNO. The downfield position of the line for $\mathrm{O_2N}N\mathrm{O}$, in which the (NO) π orbitals are extended over five atoms, may be a conjugative effect also.

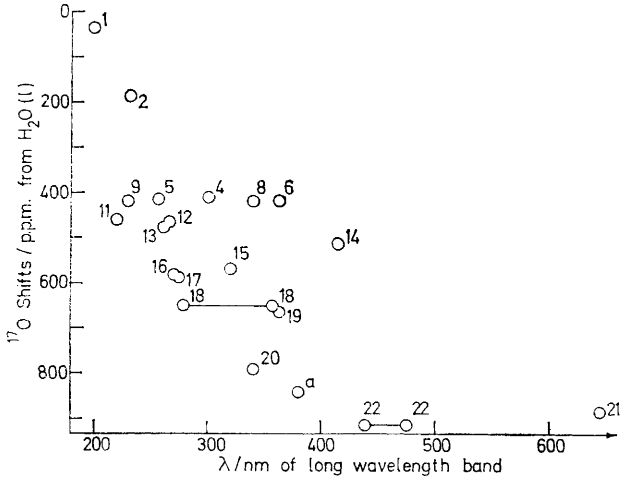

FIGURE 2 Correlation of the oxygen shifts with the inverse energy of the long-wavelength electronic absorption; the numbers refer to the Table; a, $\mathrm{Bu^tO}NO$, ref. 5.

In ^{17}O resonance, however, the conjugative (mesomeric) effect dominates, the shielding decreasing in the order NO_2^- > $\mathrm{Me_2NNO}$ > $\mathrm{MeON}O$ > $\mathrm{O_2NN}O$ > NOCl. We should of course expect the inductive effect to be less important for oxygen than for nitrogen, which is directly attached to the substituent X.

These observations begin to account for the correlation of the ^{14}N and ^{17}O shifts as shown in Figure 1. The $n \longrightarrow \pi^*$ paramagnetic circulations on oxygen and nitrogen are linked through the common π^* orbital, and also through the in-plane overlap of the n_N and n_O orbitals to give filled π' and π'^* orbitals [the relevant overlap integral, *ca.* 0·1,[10] is half as big as that for the (NO)π bond]. The circulation between these orbitals and the (NO)π^* and σ^* orbitals, in the magnetic field, deshields oxygen and nitrogen.[1]

XNO_2 *Compounds*.—In XNO_2 compounds the nitrogen resonances lie within a small region above the highest XNO line (that of NOF), and this disposition reflects the absence now of n_N electrons; deshielding is due to (NO_2) $\sigma \longleftrightarrow \pi$ circulations, as well as to $n_O \longrightarrow \pi^*$ and $n_O \longrightarrow \sigma^*$. Following the inductive effect of X, the electronic absorption is expected to move to longer wavelength and the line to move downfield in the order (NO_2F > N_2O_5 >) $RONO_2$ > O_2NNO_2 > $\mathrm{O}N\mathrm{N}$...

Among the carbonyl compounds, small groups of closely related compounds show opposite trends to those observed overall. For the group of simple aldehydes and ketones the oxygen line moves upfield (50 p.p.m.) with increasing wavelength of the $n_O \longrightarrow \pi^*$ transition, while the ^{13}C line goes down (17 p.p.m.). In increasingly dilute aqueous acetone, the ^{17}O line moves upfield (57 p.p.m.) with decreasing $n_O \longrightarrow \pi^*$ wavelength, whereas the ^{13}C line moves downfield (11 p.p.m.).[6] The scatter in Figure 2 suggests that local trends that are against the general trend may be found.

The Orbital Terms Contributing to σ_p.—The magnitude of the *p*-orbital terms in the expression for the paramagnetic shielding constant σ_p can be estimated from Pople's equations.[4] Q_{AB} Depends on the π-bonding; it is zero for singly bonded oxygen and increases to 0·43 for XNO in the sequence $R_2O < NO_3^- < NO_2^+ \sim RNO_2 \sim NO_2^- < RNO$. The resemblance to the observed sequence is to some extent fortuitous, because of the variation in Q_{AA}, which depends on the imbalance of charge in the *p* orbitals. Q_{OO} rises from 1 for XO^- to *ca.* 1·65 for RNO_2 and RNO. Thus ΣQ (the sum in the square bracket) for oxygen runs from 1·44 for NO_3^- to 2·1 for RNO in the sequence $NO_3^- < R_2O < NO_2^- < NO_2^+ \sim RNO_2 < RNO$. For oxygen shielding, then, in certain groups of compounds, changes in these constitutive terms may be commensurate with changes in ΔE. For nitrogen, Q_{NN} varies rather little, but Q_{AA} has a larger range than for oxygen.

Q_{OO} Is sensitive to inductive and mesomeric influences of the substituents. Loss of one quarter of a *p* electron from oxygen through the σ-bonds in XNO increases Q_{OO} by 12% (and electron gain decreases Q_{OO} similarly). Similar figures apply to XNO_2 compounds for loss or gain of a quarter of a *p* electron by each oxygen, which is of course more than we expect to find, since the *s* electrons are affected correspondingly, and inductive loss may be offset by conjugation. It is interesting that the change in Q_{OO} is twice as large for changes in π-electron density as for equal changes in σ-electron density. Changes in Q_{OO} are much larger than changes in Q_{NN}, for comparable polarisations.

Variation in the *p* charge density affects the radial term similarly for oxygen and nitrogen: loss of one quarter of a *p* electron, σ or π, from oxygen increases $\langle r^{-3}\rangle_{2p}$ by 6%, as estimated for Slater orbitals from the increase in effective nuclear charge.[4] (Electron gain decreases $\langle r^{-3}\rangle_{2p}$ similarly.) These changes are not negligible, for the paramagnetic shielding term relative to the bare nucleus[12] is *ca.* 800 p.p.m. for $MeNO_2$, for example. Thus with increased conjugative effect of the substituent X, the line tends to move upfield with decrease in $(\Delta E)^{-1}$, and also in Q_{AA} and $\langle r^{-3}\rangle_{2p}$; the importance of these terms perhaps decreasing in this order, for oxygen magnetic resonance. With increased (negative) inductive effect, on the other hand, the line tends to move upfield with decrease in $(\Delta E)^{-1}$, against the smaller increases in $\langle r^{-3}\rangle$ and Q_{AA}, in nitrogen magnetic resonance. But just as inductive and conjugative effects are detected in nitrogen resonance, so inductive and other effects may also be detectable in oxygen resonance, giving shift sequences in certain sets of compounds that differ from the overall trends.

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[12] W. H. Flygare and V. W. Weiss, *J. Chem. Phys.*, 1966, **45**, 2785.