28. NMR of Terminal Oxygen

Part 13^{1})

^{17}O-NMR Spectra of *C*-Nitroso Compounds, Thionitrites and NO^{+} Ion: Resonance Effects in O=N–X Compounds and Correlation with CD Spectra

by **Hans Dahn***, **Peter Péchy**^{2}), and **Rainer Flögel**

Institut de chimie organique de l'Université de Lausanne, 2, rue de la Barre, CH-1005 Lausanne

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The ^{17}O-NMR signals of four true C-nitroso compounds **1**–**4** appear at particularly low field (1550–1265 ppm), whereas the dimers (azodioxy type) resonate at *ca.* 400 ppm and the 'isonitroso compounds' (= quinone-oximes; **5** and **6**) at *ca.* 250 ppm. *S*-Nitroso compounds (= thionitrites; **8** and **9**) show shift values of *ca.* 1300 ppm, not far from C–NO; the NO^{+} ion is much stronger shielded (474 ppm). The results, together with those for higher-shielded nitroso compounds X–NO (X = RO, R$_2$N, Cl, O^{-}) are discussed in terms of *a*) resonance stabilization through n-donation from X (π-bond order, approximated by the known barriers of rotation around the X–N bond) and of *b*) electronic excitation energies ΔE. The latter are approximated by long-wave (symmetry-forbidden) UV/VIS absorptions and confirmed, where available, by the maxima of the curves of circular dichroism (CD); the CD curve of thionitrite **9** has been measured. It is found that the $\delta(^{17}O)$ values of X–NO depend both on bond order and on ΔE, which could not be separated. The higher shielding of NO^{+} compared with X–N=O is explained on the basis of anisotropy effects, which differ between sp and sp^2 systems.

Introduction. – The nitroso group is not only formally isoelectronic with the carbonyl group, but both have in common the true π-bond character, the polarization of the bond and many chemical reactions [2]. One of the most characteristic properties of the CO group is its resonance interaction with n-donors, as in amides, esters, *etc.* Analogous resonance stabilization has been found for some nitroso-containing functional groups. In N-nitrosamines, the resonance stabilization, measured by the height of the energy barrier of rotation around the N–N bond (20–25 kcal/mol [3]), is even higher than in amides; for *O*-nitroso compounds, the O–N rotation barrier is *ca.* 10 kcal/mol [3]; measurements of dipole moments and bond lengths confirm the existence of resonance-type interactions in *N*-nitrosamines [4]. In other functional groups, however, the resonance interaction of a potential n-donor with NO is less well established.

We have shown that, in contrast to ^{13}C-, ^{17}O-NMR spectroscopy is particularly useful to establish the presence of resonance interaction of CO groups with n-donors [5]. If the donor atom belongs to the second row of the periodic table (C^{-}, N, O, F), the shift values indicate the electrophilicity of the CO group and, indirectly, the degree of intervention of the n-donor: in the absence of donors, as in aldehydes and ketones, the shift value $\delta(^{17}O)$ is *ca.* 550 ppm [6], whereas n-donors cause an upfield shift, as in COOR (330 ppm), CONR$_2$ (320 ppm), COC^{-}R$_2$ (325 ppm) [7], and COO^{-} (265 ppm) [5]. Third-row atoms,

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^{1}) Part 12: [1].

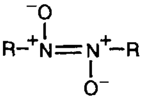
^{2}) On leave of absence from the Technical University, Budapest.

like P [8] and Si [8] [9], introduce additional influences on the shift values (see below). As in nitroso compounds analogous interactions with X exist, it would be interesting to study their effect on the $\delta(^{17}O)$ values of different types of nitroso compounds X–NO.

Among the $\delta(^{17}O)$ values of nitroso groups, those of *O*-nitroso (nitrites [10]) and *N*-nitroso (nitrosamines [11]) compounds are fairly well known, equally the shift values of NOCl and ONO^- [12]. *C*-Nitroso compounds are needed as a basis of comparison in the absence of resonance. So far, only nitrosobenzene (and its perfluoro derivative) have been measured, however, with extremely diverging results: *Furin et al.* [13] published $\delta(^{17}O) = 620$ ppm, which is surprisingly shielded. *Orrell et al.* [14] found a broad band centered at *ca.* 1524 ppm. The authors could not detect a signal due to the dimer, so they supposed that their peak also covered the signal of the latter, but this is rather improbable in view of the very different types of structure of the two compounds (see below); actually, monomers and dimers show clearly separated signals in their ^{15}N- and even in their ^{13}C-NMR spectra [14]. It appeared, therefore, necessary to make new $\delta(^{17}O)$ measurements of several *C*-nitroso compounds[3]).

As in the series of carbonyl compounds, conjugation with S (in mercapto-esters [5] [15]) shows only a slight effect on $\delta(^{17}O)$, we included measurements of S-nitroso compounds (thionitrites). Finally, we measured $NO^+BF_4^-$, in order to include the nitrosyl ion lacking an attached group X.

Results. – *C-Nitroso Compounds.* In solution, the blue or green *C*-nitroso compounds R–N=O can exist in equilibrium with their yellow or colorless dimers. As the types of N–O bonds of monomers and dimers are very different, one would expect a considerable difference of the $\delta(^{17}O)$ values. We found (*Table 1*) for 2-nitroso-2-methylpropane (**1**) in MeCN solution at 17° two peaks, at 1538 and 390 ppm. At higher temperature, when dissociation increases considerably [16] (manifest also in the deepening of the blue color of the solution), the peak at higher field disappears, showing that it belongs to the dimer. Thus the monomer has $\delta(^{17}O) = 1538$ ppm. For 17°, an estimate of the relative peak intensities (monomer/dimer *ca.* 1.3[4])) yields $K_c \approx 1.8$, in reasonable agreement with $K_c = 1.92$ known from ^1H-NMR measurements [16].



Nitrosobenzene (**2**) shows a peak at 1533 ppm. In agreement with the K_c value of *ca.* 720 [14], much higher than that of **1**, the dimer could not be expected to be visible. Our $\delta(^{17}O)$ value confirms the higher of the two published values [14]; whether the literature value of 620 ppm [13] corresponds to the dimer or to a decomposition product cannot be decided. *o*-Nitrosotoluene (**3**), in which the resonance between the arene ring and the (normally coplanar) NO group is hindered, is known to be more dimerized than **2** [17];

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[3]) **Note Added in Proof.** – Recently, the low-field value has been confirmed: C. Bleasdale, M.K. Ellis, P.B. Farmer, B.T. Golding, K.F. Handley, P. Jones, W. McFarlane, *J. Labelled Compd. Radiopharm.* **1993**, *33*, 739.

[4]) The particular conditions of measurement of ^{17}O-NMR (application of left shifts, see *Exper. Part*) do not allow a better evaluation.

Table 1. *^{17}O-Chemical Shifts of* C- *and* S-*Nitroso Compounds and Related Substances* (solvent: MeCN, unless indicated)

No.	Substance	$\delta(^{17}O)$ (N=O)[a]) [ppm]	$\delta(^{17}O)$ (other)[a]) [ppm]	T [°C]
1	$Me_3C{-}N{=}O$	1538.2	389.9[b])[c])	17
		1542.4	–	60
2	Ph–N=O	1533.4	–	40
3	$2\text{-}Me{-}C_6H_4{-}N{=}O$	1543.1	432[c])[d])	20
		1550.8	[e])	60
4	$4\text{-}Me_2N{-}C_6H_4{-}N{=}O$	1265.2	–	40
5	1,2-Naphthoquinone 1-oxime[f])		427.4 (CO) 229.1 (NOH)	40
6	1,2-Naphthoquinone 2-oxime[g])		502.4 (CO) 264.6 (NOH)	40
7	$Me_2C{=}NOH$[c])		177 (NOH)	40
8	$Ph_3CS{-}N{=}O$[h])	1293.0	[i])	35
9	$AcNHCH(COOH){-}CMe_2S{-}N{=}O$	1312.4	[i])	40
	$NO^+BF_4^-$	474.3	261.9[i])	47

[a]) Line-widths: 100–300 Hz, except for dimer of **1** 450, for **4** 450, for **5** (NOH) 550, for **6** *ca.* 1000, for **8** 700, and for **9** 450 Hz.

[b]) Dimer; $\delta(^{17}O) = 391$ ppm ($CDCl_3$, 40°).

[c]) Measured by Dr. *M.-N. Ung-Truong.*

[d]) Dimer; $CDCl_3$, 40°.

[e]) Decomposition product at 760.5 ppm.

[f]) Solvent MeCN/DMSO 2:1.

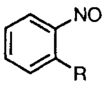
[g]) Solvent MeCN/acetone 1:3.

[h]) 0.7M in CD_2Cl_2.

[i]) See text.

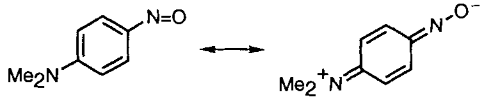
$Me_3C{-}NO$

1



2 R = H

3 R = Me



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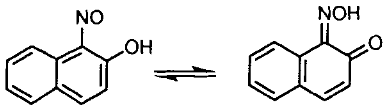

5A **5B**

6A **6B**

$Me_2C{=}NOH$

7

$Ph_3CS{-}NO$

8

$AcNH{-}CH(COOH){-}CMe_2S{-}NO$

9

however, as, for solubility reasons, a lower concentration had to be measured, we could not detect a signal of the dimer in our standard solvent MeCN, but only the monomer at 1543 ppm (20°). A $CDCl_3$ solution showed a signal at 432 ppm, presumably due to the dimer. At higher temperature in MeCN, the peak of an unidentified decomposition product appeared at 760 ppm.

In *N,N*-dimethyl-4-nitrosobenzeneamine (**4**), where the electron-donating Me_2N group is expected to increase the shielding of O (and which does not dimerize), the NO signal is found at 1265 ppm.

The *o*- and *p*-nitrosophenols and -naphthols present a special case: they can exist in the tautomeric form of quinone-monoximes. For *p*-benzoquinone monoxime, the absence of the tautomer *p*-nitrosophenol has been demonstrated by several spectroscopic techniques [18], whereas, for the 1,2-naphthoquinone monoximes, the presence of the nitroso forms **5A**, **6A** in solution is controversial [19]. We have measured the ^{17}O-NMR spectra of 1,2-naphthoquinone-1-oxime **5** and -2-oxime **6** (in MeCN) and found no signal in the region between 600 and 1400 ppm, where the signal of a NO group (**5A**, **6A**) would be expected. The signals found at 427 ppm (**5**) and 502 ppm (**6**) are not far from those of CO groups of ketones and quinones, *e.g.* 1,4-naphthoquinone, 572 ppm [20]; the strong H-bridge between =NOH and =O would be expected to increase the shielding of the latter [21]. The oxime groups of **5B** and **6B** manifest themselves by signals at 229 ppm (**5**) and 265 ppm (**6**); we found for acetone oxime (**7**) a signal at 177 ppm, other oximes have been found at 170–195 ppm [22]. The difference between the 1-oxime **5B** and the 2-oxime **6B** can be attributed to differences in chelation (1 > 2), manifest also in solubility and in IR spectra [19].

S-Nitroso Compounds (Thionitrites). Many thionitrites are rather unstable compounds [23] which would not stand the conditions of ^{17}O-NMR measurement. *S*-Nitrosotriphenylmethanethiol (*S*-trityl-thionitrite, **8**) [24] could be measured in a rather concentrated CD_2Cl_2 solution at 35°: it showed a signal at 1293 ppm. In more dilute DMSO solution and after correspondingly longer accumulation time, the signal of an unidentified decomposition product (perhaps a CO compound) appeared at 497 ppm. *N*-Acetyl-*S*-nitrosopenicillamine (**9**) [25] is one of the most stable thionitrites. As it shows rather low solubility in the O-free unpolar solvents necessary for ^{17}O-NMR measurements, we had to enrich its NO group, in order to be able to apply a sufficient number of scans before decomposition would catch up; the COOH and CONH groups were not enriched in the process. By measuring a saturated solution containing undissolved blue crystals of **9**, it was possible to follow the peak of the intact compound at 1312 ppm over several hours (MeCN solution at 40°). On the other hand, when working in more dilute solution (*ca.* 3 mg/ml), new peaks emerged after several hours from the fading solution of **9**. The most prominent was that of (enriched) $H_2{}^{17}O$ at −9 ppm (literature value of H_2O in MeCN: −11 ppm [6b]), which thus has been formed from the O-atom of the enriched NO group. Other peaks appeared (and later disappeared) at 819 and 600 ppm; the former might be due to a *N*-nitrosamine (or nitrosamide) formed by NO transfer [26]. A peak appearing at 263 ppm after long accumulation might be that of the (unlabelled) COOH group.

^{17}O-Enrichment of **9** was achieved by nitrosating *N*-acetylpenicillamine in $H_2{}^{17}O$ (10% ^{17}O). It is known that the nitrosating species ($H_2NO_2^+$, NO^+, NOCl, *etc.*) formed from $NaNO_2$ and aqueous acid are in rapid equilibrium with water and thus incorporate oxygen tracer, which they transfer to the nitrosated substrate. It is necessary to choose nitrosation conditions under which the O-exchange between (labelled) water and (unlabelled) HNO_2, *via* attack of the nitrosating electrophile on the nucleophile H_2O, is more rapid than its attack on the (more nucleophilic) substrate. To achieve this, one has to generate the most active nitrosating species, which, being least discriminating, will prefer the abundant $H_2{}^{17}O$ over the more nucleophilic but less abundant substrate; under the conditions chosen (strongly acidic solution, presence of Cl^-), one can estimate that v(exchange)/v(nitrosation) $\approx 10^5$, *i.e.* complete incorporation of the tracer [27]. Under these conditions, COOH and RNHCO groups do not exchange their O-atoms with water.

Nitrosonium Tetrafluoroborate. This compound, only slightly soluble, needed 15 h of spectral accumulation to give clear signals. The main peak was found at 474 ppm. A smaller peak at 262 ppm increases in intensity upon standing; it might be due to AcOH (254 ppm [10]) formed from the solvent.

Discussion. – With shift values of 1530–1550 ppm, the O-atoms of *C*-nitroso compounds are among the most deshielded so far measured[5]). It is significant that the NO O-atoms of NOX are much more deshielded than those of the isoelectronic CO compounds RCOX: *e.g.* RN=O *ca.* 1540 ppm *vs.* RCH=O *ca.* 590 ppm, RONO 800 ppm [10] *vs.* RCOOR′ *ca.* 350 ppm [6a].

In the absence of published calculations (IGLO, LORG), the shift data can be discussed in terms of the *Karplus-Pople* equation (*Eqn. 1*) [30]

$$\sigma^p = -\text{const.} \cdot \Delta E^{-1} \cdot r^{-3} \cdot \Sigma Q \tag{1}$$

where σ^p represents the paramagnetic (*i.e.* deshielding) contribution to the total shielding, ΔE is the electronic excitation energy, empirically approximated by the longest-wave (symmetry-forbidden) absorption in the UV/VIS spectrum, r is the radius of the p orbital at the atom measured, and ΣQ the charge density-bond order matrix, approximated by the π-bond order at the measured atom. The equation shows why atoms in π-bonds are particularly deshielded, *via* high bond order and/or *via* low-energy $n \rightarrow \pi^*$ transitions. It must be stressed, however, that the 3 terms of *Eqn. 1* are certainly not independent from one another, only rarely has it been possible to separate them on an experimental basis [31].

In the case of the shift difference between RNO and RCHO, the importance of the influence of the ΔE term is immediately clear: the *C*-nitroso compounds are blue, with $n \rightarrow \pi^*$ bands at 650–750 nm [32], whereas aldehydes show $\lambda(n \rightarrow \pi^*)$ at *ca.* 280 nm [33]; the lower value *of* ΔE causes diminished shielding.

Influence of X in NOX. Between the nitrite anion $ON{-}O^-$ (650 ppm) and *C*-nitroso compounds ON–C (1540 ppm) the $\delta(^{17}O)$ values of the NO group extend over a range of *ca.* 900 ppm. The shift range of the corresponding isoelectronic CO groups, *i.e.* COO^- anions (*ca.* 265 ppm) and aldehydes (*ca.* 550 ppm), is significantly narrower, though still quite large[6]). There are, however, CO compounds with considerably smaller (disilylketone $\delta(^{17}O) = 956$ ppm [9]; see below) and larger shielding (methylisocyanate, 84 ppm [6a]).

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[5]) Only the terminal O-atom of O_3 (1598 ppm [28]) and the two O-atoms of the (electronically comparable) Fe–O–O groups in Fe-dioxygen complexes (*e.g.* porphyrinedioxygen, 2488 and 1755 ppm [29]) appear at still lower field.

[6]) This high structure sensitivity, common to N=O and C=O, contrasts with that of O bound to P and S, and is characteristic for true π_p bonds; for the semipolar bonds $P^+{-}O^-$ and $S^+{-}O^-$ (previously often considered as π_d bonds), the $\delta(^{17}O)$ values are found at higher field (0 to 100 ppm) and within a narrower range [6b] [34].

Donor groups X conjugated with CO in RCOX ($X = RS < RO < R_2N < O^-$) increase the shielding at the carbonyl O-atom *via* resonance $X{-}CR{=}O \leftrightarrow X^+{=}CR{-}O^-$, which diminishes the π-bond order of the C–O bond. The same would be expected for resonance in $X{-}N{=}O \leftrightarrow X^+{=}N{-}O^-$. As mentioned above, the measured rotational barriers [3] around the X–N bond ($X = Me < Ph < RO < R_2N$) show that this resonance exists. *Table 2* resumes the shift data of a variety of XNO compounds. The data show the trend that increasing the rotational barrier X–N by resonance, and thus diminishing the π-bond order of NO, the shielding of O increases. The resonance-donating power of the group X can also tentatively be represented by its *Taft*-type substituent constant σ_R; actually a plot of $\delta(^{17}O)$ *vs.* σ_R^0 is reasonably linear ($r = 0.95$). These are indications that the bond-order term of *Eqn. 1* influences the shielding, though the correlation is less strict than in the case of the CO compounds RCOX [5].

Table 2. *^{17}O-NMR and $^{14,15}N$-NMR Shift Data, CD Maxima and Longest Wavelength UV/VIS Absorptions, and Rotational Barriers of Nitrosyl Compounds*

Compound	$\delta(^{17}O)$ [ppm]	$\delta(^{14,15}N)$ [ppm]	$\lambda(n \to \pi^*)$a) [nm]	Rotational barrier [kcal/mol]
RR′R″CNO	1538	590 [45]	680* [33]	
PhNO	1533	530 [45]	755 [32]	7.7 [42]
$4\text{-}Me_2NC_6H_4NO$	1265	386 [43]	775 [32]	13.0 [42]
RSNO	1300	452 [45]	600* [24]	
ClNO	915 [12]	222 [36]	460b)	
RONO	800 [10]	190 [45]	355* [33]	10.5 [3]
R_2NNO	670 [11]	155 [45]	365* [33]	23 [3]
O^-NO	650 [12]	229 [37]	357 [36]	
NO^+	474	–3 [45]	< 210 [36]	

a) Maxima confirmed by data for CD, this work or [35], are marked by *.

b) Data from M.J. Collis, F.P. Gintz, D.R. Goddard, E.A. Hebdon, G.J. Minkoff, *J. Chem. Soc.* **1958**, 438; J. Jander, R.N. Haszeldine, *ibid.* **1954**, 912; see also [36].

On the other hand, it is evident from *Fig. 1* and the data of *Table 2* that the shift values are strongly dependent upon the value of λ of the longest-wave (forbidden) UV/VIS absorption: in going from *C*-nitroso compounds to nitrite anion, the $\delta(^{17}O)$ values change by a factor of 2.4. As many nitroso compounds show multiple long-wave absorptions, and as the absorption bands corresponding to symmetry-forbidden transitions are often weak and/or ill-defined, it would be useful to check the choice of the magnetically active transition by an independent method. This is, in principle, possible on the basis of the fact that the same symmetry-forbidden electron transition must be operative for NMR (*Eqn. 1*) as well as for other magneto-optical phenomena, including in particular CD spectroscopy. The λ_{max} values for X = alkyl, RO, and R_2N are close to those given in [35] for the maxima of the corresponding CD curves (*Table 2*). We have completed the series by measuring the CD spectrum of chiral D-**9**: it shows the longest-wavelength CD band at 606 nm, the longest-wavelength UV/VIS absorption at 593 nm (see below). When $\delta(^{17}O)$ is plotted *vs.* the CD maxima and/or the $\lambda(n \to \pi^*)$ values of *Table 2* (excluding **4**, see below), a linear dependence is visible (*Fig. 1*), with the slope of 2.3 ($r = 0.98$), demonstrating the influence of the ΔE term upon the chemical shifts $\delta(^{17}O)$.

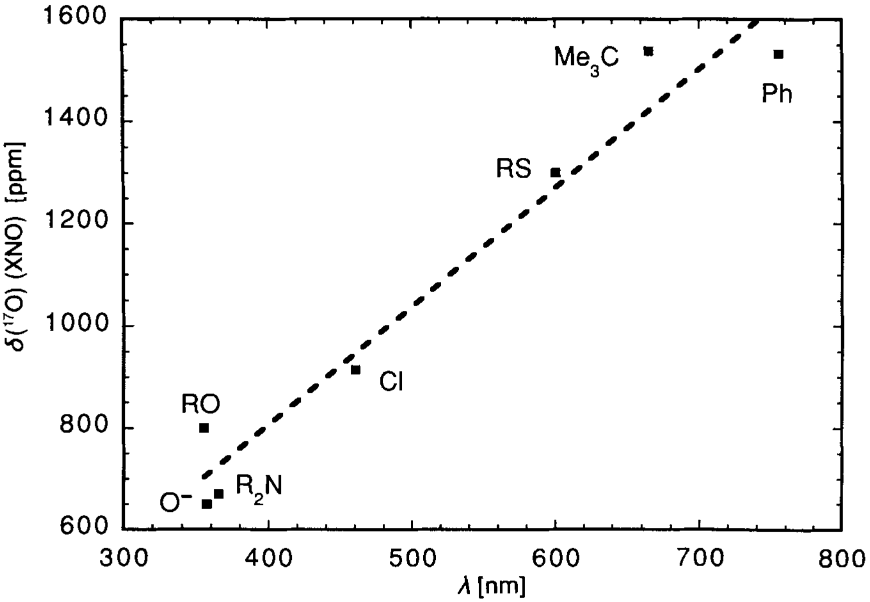

Fig. 1. *Plot of* δ(*^{17}O*) vs. *CD maxima and* λ(*n*$\rightarrow\pi^*$) *of nitroso compounds X–NO*

The importance of the ΔE term for the shift values can be confirmed by ^{14,15}N-NMR, as $\delta(^{14,15}N)$ must, of course, depend upon the same ΔE term as $\delta(^{17}O)$. For the ^{14,15}N-NMR chemical shift values of N–O compounds, *Mason* and coworkers [36] had established a linear dependence of $\delta(^{14,15}N)$ (NOX) upon $\lambda(n\rightarrow\pi^*)$; using the data of *Table 2* (excluding **4**), we find the slope $\delta(^{14,15}N)/\lambda = 1.0$ ($r = 0.94$). This is much smaller than the value of 2.3 found for $\delta(^{17}O)/\lambda$; *i.e.* $\delta(^{14,15}N)$ is much less sensitive to variations of structure than $\delta(^{17}O)$. For these compounds, the ratio of the δ/λ slopes of ^{17}O and ^{14,15}N (which should equal the slope $\delta(^{17}O)/\delta(^{14,15}N)$ of a correlation line of $\delta(^{17}O)$ *vs.* $\delta(^{14,15}N)$) is 2.3. This is a significant figure: applying *Eqn. 1* to both ^{17}O-NMR and ^{14,15}N-NMR, the ΔE term must be identical; if one admits that changes in the bond-order term ΣQ are negligible, $\delta(^{17}O)/\delta(^{14,15}N)$ represents $(r_O^{-3})/(r_N^{-3})$, that is the ratio of the mean inverse cubes of the radii of the 2p orbitals on O and N, respectively [12] [37]. This value is known from microwave spectroscopy: 1.75 [38]; we cannot decide whether the difference between this expected value and our result (2.3) is significant or not.

In conclusion, the $\delta(^{17}O)$ values of the nitroso compounds are influenced both by the bond order and the electronic excitation energy term of *Eqn. 1*; it is not possible to separate them on an experimental basis. This differs from the situation with CO groups in RCO–X: when X = R_2C^-, R_2N, RO, or F, the variation of $\lambda(n\rightarrow\pi^*)$ is smaller than for NO in O=N–X, and thus the influence of the ΔE term appears less marked. On the other hand, when X is a third-row element like Si or P, strong red-shifts in the UV/VIS spectra of RCO–X accompany strong deshielding in ^{17}O-NMR [9].

The Nitrosonium Ion. It is striking to find the oxygen of free NO^+ so much shielded, more than any of the nitroso compounds measured. The same observation can be made for N-NMR of NO^+: $\delta(^{14,15}N) = -3$ ppm (not influenced by the counterion), *i.e.* at

> 200 ppm higher field than covalent NO compounds (*Table 2*). Using *Eqn. 1*, a possible explanation of this shielding might be seen in the loss of low-energy electronic excitation (NO^+ shows $\lambda_{max} < 210$ nm, *Table 2*). As to the π-bond order term of *Eqn. 1*, however, the triple bond corresponding to the resonance formula

$$N^+{=}O \leftrightarrow N{\equiv}O^+$$

would predict a strong deshielding, which is contrary to observation. The situation of NO^+ might be compared with that of the acyl cations RCO^+, $\delta(^{17}O) = 330$ ppm [39], which are also much more shielded than the corresponding aldehydes RCHO and methyl ketones RCOMe ($\delta(^{17}O) \approx 550$ ppm); in this latter case neither the bond term nor the electronic excitation term allow to explain the high shielding.

An explanation can be based on the fact that $^+N{=}O$, through its resonance formula $:N{\equiv}O:^+$, is isoelectronic with $CH{\equiv}CH$. The shift values of the latter, in ^{13}C- as well as in ^1H-NMR, are intermediate between those of $CH_2{=}CH_2$ and $CH_3{-}CH_3$, *e.g.* $CH_3{-}CH_3$, $\delta(C) = 5.7$ ppm; $CH_2{=}CH_2$, $\delta(C) = 123.3$ ppm; $CH{\equiv}CH$, $\delta(C) = 71.9$ ppm [40]. This is often explained in terms of differences of magnetic anisotropy [40]: whereas in the sp^2 system the field-induced electron motion is parallel to the plane of the atoms, it is perpendicular to the axis of atoms in the sp system. Though this explanation seems not to be universally accepted [41], it might be useful to explain the difference of shielding between $X{-}N{=}O$ (double bond) and $:N{\equiv}O^+$ (triple bond), as well as that between $R{-}CH{=}O$ and $R{-}C^+{=}O \leftrightarrow R{-}C{\equiv}O^+$: in both cases the triple-bond system is found more shielded than the double bond.

Substituent Effect in Nitrosoarenes. N,N-Dimethyl-4-nitrosobenzeneamine is characterized by an important resonance **4A**↔**4B**, manifest by an increase of the rotational barrier around the C–N bond: **1**: 7.7 kcal/mol, **4**: 13 kcal/mol [42]. As expected, this resonance increases the shielding of the NO group: **1**: $\delta(^{17}O) = 1533$ ppm, **4**: 1265 ppm. The increase of shielding in ^{17}O-NMR parallels that in $^{14,15}N$-NMR: **1**: $\delta(^{14,15}N) = 530$ ppm [14], **4**: 386 ppm [43]. As the difference in the electronic absorption seems to be rather small (**1**: 755 nm, **4**: 775 nm [32]), one can admit that the bond-order term of *Eqn. 1* is more important here. (For this reason, the values of **4** have been excluded from the correlation mentioned above.)

C-*Nitroso Dimers.* Due to their azodioxy formula $R{-}N(O){=}N(O){-}R$ ((*E*) and (*Z*)), the N–O group of the dimers, containing no π_p bond, is very different from that of true (monomeric) nitroso compounds $R{-}N{=}O$; this is immediately apparent in the electronic spectra, and in ^{17}O-NMR. The NO groups of the dimers correspond to $N^+{-}O^-$ as found in azoxy compounds, nitrones, and even *N*-oxides, a resemblance borne out by the ^{17}O-shift values: nitroso dimers $\delta(^{17}O) = 390$ ppm (dimer of **1**) and 432 ppm (dimer of **3**); azoxybenzene $Ph{-}N(O){=}N{-}Ph$: 456 [13]; nitrone $Ph{-}N(O){=}CH{-}Ph$: 377 [44]; pyridine *N*-oxide: 349 [6a]; these shift values show more than 1000 ppm higher shielding than those of the nitroso monomers. The $^{14,15}N$-NMR-shift values exhibit the analogous situation: dimer of **1** has $\delta(^{14,15}N) = -65$ ppm, *ca.* 600 ppm more shielded than **1**, and close to azoxybenzene (−57 ppm) and other comparable compounds [45].

CD Spectrum of Thionitrite **9**. The CD spectrum of the D-enantiomer of compound **9**, prepared from (natural) D-(*S*)-acetylpenicillamine by the same method as the racemate [25], exhibits in the VIS part of the spectrum five maxima, at 606, 582, 559, 540, and 521 nm; the first, third, and fifth are positive, the two others negative (*Fig. 2*). The curve

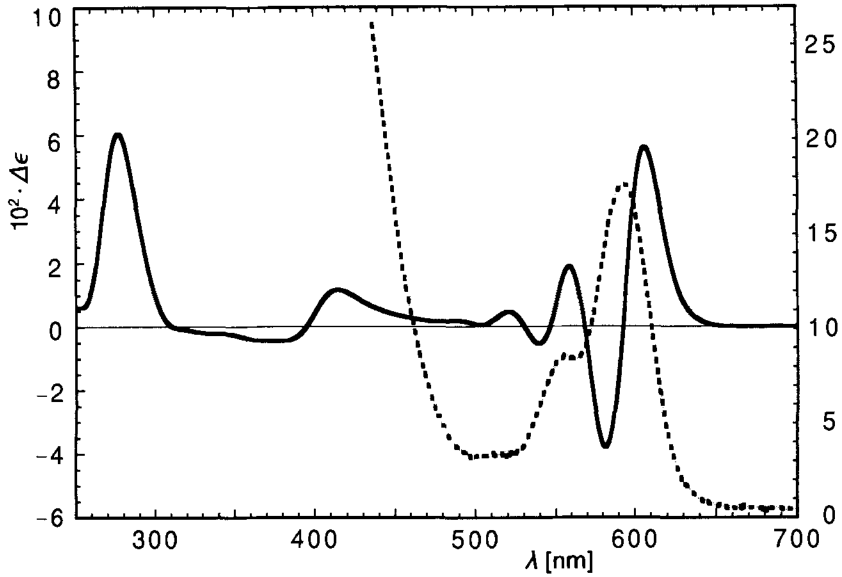

Fig. 2. *CD Spectrum* (——, left scale) *and VIS absorption spectrum* (····, right scale) *of* N-*acetyl*-S-*nitroso*-D-*penicillamine* (D-**9**, MeCN solution, 25°)

exhibits qualitatively a striking resemblance with those of *C*-nitroso compounds, only slightly displaced to lower wavelengths [46]. In the UV/VIS spectrum the absorptions corresponding to the CD signals at 601 and 582 nm are not resolved, but appear as a single band at the medium wavelength 593 nm ($\varepsilon = 19$; even the first derivative of the UV/VIS curve shows no sign of a substructure, nor do deconvolution procedures). The CD band at 559 nm appears in the UV/VIS spectrum as a shoulder (555 nm, $\varepsilon = 8$). The assignment of these bands to electronic transitions, generally $n \rightarrow \pi^*$, is similar to those of *C*-nitroso compounds [32] [33], and has been discussed in some detail in [36]. At lower wavelength, a broad CD band at 413 nm ($\Delta\varepsilon = +1.3 \cdot 10^{-2}$) might correspond to the UV absorption found at 342 nm (thionitrites absorb at *ca.* 340 nm [24]), and a marked CD signal at 272 nm ($\Delta\varepsilon = +6.1 \cdot 10^{-2}$) is close to the UV absorption of the solvent MeCN. For the correlation with $\delta(^{17}O)$, we have used the mean value of 600 nm of the longest-wavelength signals, which, as CD proves, is magnetically active and thus efficient for NMR.

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Experimental Part

^{17}O-NMR Spectroscopy. ^{17}O-NMR Spectra were recorded on a *Bruker WH-360* spectrometer equipped with a 10-mm probe at 48.8 MHz in the *Fourier* transform (FT) mode without lock. System control, data acquisitions, and data managements were performed by an *Aspect-2000* microcomputer. The instrumental settings were as follow: spectral width 50000 Hz (1025 ppm); 2-K data points; pulse width 33 µs; acquisition time 20 ms; preacquisition delay 5 µs; 1.4–2.3M scans; measurements were made with sample spinning (27 Hz). To suppress base line roll

from acoustic ringing, an even number (28–32) left-shifts (LS) were applied to the FID signal; the latter was zero-filled to 8-K words, and exponentially multiplied with a 100-Hz line-broadening factor (LB) before being subjected to the FT. The chemical shifts are reported relative to $\delta(^{17}O)(H_2O) = 0.0$ ppm; dioxane ($\delta(^{17}O) = 0$ ppm) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shift values is *ca.* ±1 ppm (±0.2 ppm within the same series).

CD Spectra were measured on a *Jobin-Yvon CD6* instrument at 25°, UV/VIS spectra on a *Varian-Cary 5* spectrometer.

Triphenylmethyl Thionitrite (S-*Nitroso-triphenylmethanethiol*, **8**) was prepared from triphenylmethanethiol (*Fluka*, recrystallized) and *t*-butyl nitrite [24] [47].

N-*Acetyl*-S-*[^{17}O]-nitroso*-D-*penicillamine* **9** [25]. To a soln. of 48 mg (0.25 mmol) of *N*-acetyl-D-penicillamine (*Fluka*) in 0.5 ml of MeOH, 0.5 ml of (normal) H_2O, and 0.05 ml of conc. HCl, a soln. of 35 mg (0.5 mmol) of $NaNO_2$ in 0.5 ml of $H_2{}^{17}O$ (10% ^{17}O) and 0.05 ml of conc. H_2SO_4 was added. After stirring 30 min, the green crystals were isolated, thoroughly washed with (normal) H_2O, and dried. For ^{17}O-NMR, 10 mg of **9** were suspended in 3 ml of anh. MeCN.

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