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Oxygen-17 Nuclear Quadrupole Double-Resonance Spectroscopy. 3. Results for N–O, P–O, and S–O Bonds[1]

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Abstract: The ^{17}O nuclear quadrupole resonance (NQR) spectra in natural abundance in a series of compounds containing N–O, P–O, and S–O bonds have been measured at 77 K via a field-cycling double-resonance technique. Compounds studied are nitrobenzene and seven substituted nitrobenzenes: γ-picoline *N*-oxide, imidazolium nitrate, triphenyl phosphate, triphenylphosphine oxide, diphenyl sulfoxide and bis(*p*-chlorophenyl) sulfoxide, diphenyl sulfone, and bis(*p*-chlorophenyl) sulfone. The quadrupole coupling constants range from a high value of 15.63 MHz for γ-picoline *N*-oxide to a low value of 3.825 MHz for triphenyl phosphate. The ^{17}O data are insensitive to meta or para substituents in the nitrobenzenes except where hydrogen bonding is introduced, as in *p*-nitroaniline. The data for the compounds containing P–O and S–O bonds point to the existence of substantial π-bond order, which appears to vary in the order $(C_6H_5O)_3PO > (C_6H_5)_2SO_2 \approx (C_6H_5)_3PO > (C_6H_5)_2SO$.

Introduction

In the first paper of this series we reported ^{17}O ($I = {}^5\!/_2$) nuclear quadrupole double-resonance spectra for a variety of organic carbonyl compounds.[3] The results of that work showed that the NQR data are a sensitive function of the electronic environment about oxygen. In this paper we report the ^{17}O nuclear quadrupole double-resonance spectra in natural abundance (0.037%) for some compounds in which oxygen is singly attached to nitrogen, phosphorus, or sulfur. The quadrupole coupling constants in these systems vary over a wide range. By use of the Townes–Dailey model, the results can be reasonably interpreted in terms of variations in occupancies of the valence orbitals on oxygen.

Experimental Section

The techniques employed are essentially those described in the previous papers.[3,4] All samples, examined as powered solids or frozen liquids at 77 K, were obtained from commercial sources as materials of high purity and were used without further purification.

Results

Nitrogen–Oxygen Compounds. The observed ^{17}O NQR frequencies of nitrobenzene and several substituted nitrobenzenes are given in Table I, along with data for γ-picoline *N*-oxide and imidazolium nitrate. In compounds 1 and 5 only two absorptions are observed, as expected for a single type of oxygen. Signals due to the aldehyde oxygens are observed in *m*- and *p*-nitrobenzaldehydes (Table I) at frequencies expected for this functional group.[3]

In imidazolium nitrate only one pair of oxygen signals was seen with reasonably good signal to noise. Other much weaker signals were observed but could not be well characterized.

Table I. Oxygen-17 NQR Data at 77 K for Oxygen Unicoordinated to Nitrogen

compd	$\nu({}^5\!/_2-{}^3\!/_2)^a$	$\nu({}^3\!/_2-{}^1\!/_2)$	e^2Qq/h^b	η
nitrobenzene	3714	2573	13.09	0.576
p-chloronitrobenzene	3720	2565	13.10	0.571
m-chloronitrobenzene	3727	2575	13.13	0.573
m-dinitrobenzene	3725	2560	13.10	0.572
p-dinitrobenzene	3720	2565	13.10	0.571
m-nitrobenzaldehyde[c]	3752	2566	13.17	0.551
p-nitrobenzaldehyde[d]	3758	2560	13.12	0.574
	3692	2590		
p-nitroaniline	3390	2745	12.57	0.743
	3549	2803		
imidazolium nitrate	3468	2795	12.57	0.747
γ-picoline *N*-oxide	4594	2631	15.63	0.328

[a] The notation of transition frequencies used is that employed in ref 3 and 4. Units are in kHz. [b] Units are in MHz. [c] Aldehyde oxygen transitions are at 3093 and 1929 kHz; $e^2Qq/h = 10.70$ MHz, $\eta = 0.452$. [d] Aldehyde oxygen transitions are at 3072 and 1910 kHz; $e^2Qq/h = 10.62$ MHz, $\eta = 0.449$.

Table II. Oxygen-17 NQR data at 77 K for Oxygen Bonded to Phosphorus or Sulfur

compd	ν-$({}^5\!/_2-{}^3\!/_2)^a$	ν-$({}^3\!/_2-{}^1\!/_2)^a$	e^2Qq/h^b	η
triphenyl phosphate	2673 (1)	1748 (1)	9.322 (2)	0.510 (1)
	2526 (1)	1924 (1)	9.060 (2)	0.683 (1)
	2526 (1)	2023 (1)	9.146 (2)	0.740 (1)
	1145 (10)	585 (10)	3.825 (30)	0.098 (30)
triphenylphosphine oxide	1403 (2)	708 (1)	4.684 (2)	0.085 (15)
diphenyl sulfoxide	2804 (1)	1498 (1)	9.446 (2)	0.232 (2)
bis(*p*-chlorophenyl) sulfoxide	2821 (1)	1498 (1)	9.494 (2)	0.221 (2)
diphenyl sulfone	2003 (1)	1056 (1)	6.734 (2)	0.209 (2)
bis(*p*-chlorophenyl) sulfone	1968 (1)	1063 (1)	6.642 (2)	0.252 (2)

[a] Transition frequencies are in kHz. [b] Quadrupole coupling constants are in MHz.

Most of the nitrobenzenes exhibit NQR signals for only one crystallographically distinct oxygen, which is consistent with the reported crystal structures for nitrobenzene,[5] *m*-chloronitrobenzene,[6] *m*-dinitrobenzene,[7] and *p*-dinitrobenzene.[6] Two sets of closely spaced ^{17}O NQR signals are seen for *p*-nitrobenzaldehyde. The quadrupole coupling constant and asymmetry parameter listed in Table I is an average of the values calculated for the two different sites. Similarly, in *p*-nitroaniline, two sets of ^{17}O transitions were observed, consistent with the crystallographic data.[9] In this case there is a hydrogen bonding interaction between the nitro oxygens and the N–H bonds of the amino groups of adjacent molecules. The amino nitrogen–oxygen distances are different, 3.14 and 3.07 Å. Though the two N–O bonds of the nitro group are of the same length within experimental error, the ^{17}O NQR data clearly reflect a difference in the hydrogen bonding interaction for the two oxygens. The single value of e^2Qq/h and η listed in Table I is an average of the values for the two nonequivalent sites.

With the exception of *p*-nitroaniline, in which hydrogen bonding

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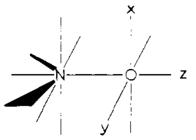

Figure 1. Axis system in N–O containing compounds.

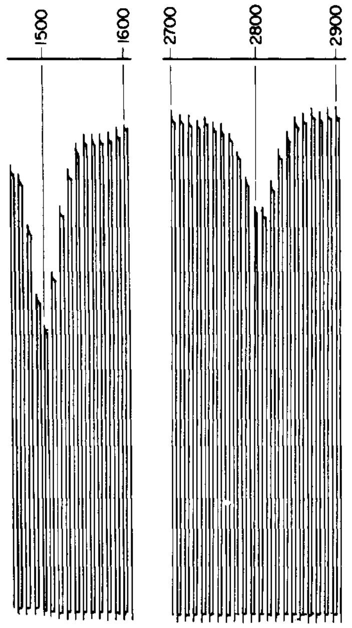

Figure 2. Natural abundance ^{17}O NQR spectrum for diphenyl sulfoxide, 77 K. Frequencies are given in kHz. Spectral points here are taken at 10-kHz intervals.

plays a role, the ^{17}O NQR data for all the nitrobenzene compounds are surprizingly alike. The average coupling constant is 13.12 ± 0.03 MHz, and the asymmetry parameter is 0.570 ± 0.003.

Phosphorus–Oxygen and Sulfur–Oxygen Compounds. The ^{17}O NQR data for oxygen bonded to phosphorus or sulfur are listed in Table II. Except for triphenyl phosphate the spectra are simple. In each case two signals are observed, which correspond to the two allowed ^{17}O NQR transitions. The spectrum of diphenyl sulfoxide, shown in Figure 1, is typical of those obtained. By contrast, the spectrum of triphenylphosphate is complicated. Two weak signals appear at 1145 kHz and 585 kHz; the signals at 1748, 1924, 2023, 2526, and 2673 kHz are comparatively stronger. The pair of weak signals can be assigned to the singly connected oxygen bound to phosphorus. Since the proton–oxygen distances for this oxygen are likely to be longer than for the other oxygens, the cross-relaxation rates should be slower, with a resultant weaker signal for a given irradiation period.[4,10] The crystal structure for triphenyl phosphate reveals that the three phenoxy oxygens are nonequivalent.[11,12] The three observed P–O distances for these oxygens are 1.549, 1.554, and 1.599 Å. Two of the phenoxy oxygens are quite similar, while the third is more distinctly different. It seems reasonable to assign the 1748-, 1924-, and 2023-kHz signals to the $\nu(^3/_2 - {}^1/_2)$ transitions of the three different oxygens, because they all have identical intensities. The intensity of the 2526-kHz signal is noticeably stronger than the 2673-kHz signal; it appears that there are two overlapping transitions at the lower frequency. Thus the phenoxy oxygen transitions may be paired as indicated in Table II. It seems reasonable to associate the 2673–1748-kHz pair of signals with the oxygen having the longest P–O bond length, but nothing definitive can be said on the point.

Analysis of Data. In a previous paper we applied the Townes–Dailey model[13] to analysis of ^{17}O NQR data in organic carbonyls.[3] A similar approach can be used in treating data presented in Tables I and II for singly connected oxygen bound to N, S, or P. In the nitrogen compounds the axis system is as shown in Figure 2; the oxygen p_x orbital is oriented for interaction with the p_π orbital of nitrogen. The description of the oxygen valence orbitals is the same as that presented earlier.[3] The components of the electric field gradient (EFG) tensor are expressed in the molecular axis system by eq 1, where p_π and p_σ represent

$$\begin{aligned} q_{zz} &= [-1 - p_\pi/2 + p_\sigma(1 - \alpha^2) + 2\alpha^2]q_{210} \\ q_{yy} &= [2 - p_\pi/2 - p_\sigma(1 - \alpha^2)/2 - \alpha^2]q_{210} \qquad (1) \\ q_{xx} &= [-1 + p_\pi - p_\sigma(1 - \alpha^2)/2 - \alpha^2]q_{210} \end{aligned}$$

the populations of the oxygen p_x orbital and the hybridized orbital employed in the σ bond to N, respectively. The quantity q_{210} is the field gradient due to a single oxygen 2p electron; the quantity e^2Qq_{210}/h has the value 20.9 MHz.[3,14] The fractional s character in the σ orbital is represented as α^2. If we let $p_\sigma^0 = p(1 - \alpha^2) + 2\alpha^2$, eq 1 is expressed in terms of the two unknown quantities p_σ^0 and p_π, as in eq 2. We defer the question of s character for the moment.

$$\begin{aligned} q_{zz}/q_{210} &= -1 - p_\pi/2 + p_\sigma^0 \\ q_{yy}/q_{210} &= 2 - p_\pi/2 - p_\sigma^0 \qquad (2) \\ q_{xx}/q_{210} &= -1 + p_\pi - p_\sigma^0 \end{aligned}$$

There are six possible assignments of the field gradient principal axes X, Y, and Z to the molecular x, y, and z axes, and for each of these, two possible signs for e^2Qq_{ZZ}. For each of the 12 possible cases values can be calculated for p_π and p_σ^0, on the basis of ^{17}O EFG parameters in a given aromatic nitro group (Table III).

Table III. Analysis of the ^{17}O Data of Nitro Group in Nitrobenzene for All the Possible Orientations of Principal Axes X, Y, and Z Relative to the Molecular Axis System x, y, and z[a]

assumed rel[b] efg components	sign of e^2Qq	p_π	p_σ^0
(1) $zz \geqslant yy \geqslant xx$	+	2.238	2.746
(2) $zz \geqslant xx \geqslant yy$	+	1.762	2.508
(3) $zz \geqslant yy \geqslant xx$	–	1.762	1.254
(4) $zz \geqslant xx \geqslant yy$	–	2.238	1.492
(5) $yy \geqslant xx \geqslant zz$	+	1.254	1.492
(6) $yy \geqslant zz \geqslant xx$	+	1.492	1.254
(7) $yy \geqslant xx \geqslant zz$	–	2.746	2.508
(8) $yy \geqslant zz \geqslant xx$	–	2.508	2.746
(9) $xx \geqslant yy \geqslant zz$	+	2.746	2.233
(10) $xx \geqslant zz \geqslant yy$	+	2.508	1.762
(11) $xx \geqslant yy \geqslant zz$	–	1.254	1.762
(12) $xx \geqslant zz \geqslant yy$	–	1.492	2.238

[a] $e^2Qq/h = 13.10$ MHz, $\eta = 0.570$. [b] Absolute values.

When the appropriateness of each assignment is evaluated, it should be kept in mind that the orbital populations deduced from a Townes–Dailey analysis of the NQR data are roughly equivalent to atomic orbital populations based on a Mulliken-type population analysis of the ground-state molecular wave function.[15] One thus expects that p_π and p_σ^0 should not exceed 2. Further, since in simple valence bond terms each N–O bond of the nitro group has a 0.5 π-bond order, p_π should be on the order of 1.5. Because oxygen is more electronegative than nitrogen, it is reasonable to expect that p_σ^0 should be somewhat larger than 1.0. Only cases 3, 5, 6, and 11 of Table III are possibilities, and of these case 6 appears most in accord with naive expectations. However, it will be necessary to carry out an ^{17}O NQR study of an oriented single crystal to unambiguously determine the correct choice of EFG tensor axes.

In γ-picoline N-oxide there is little question of the orientation of the EFG components. The extent of π bonding with the pyridine ring is not large. The nitrogen–oxygen interaction is of a class often referred to as semipolar; that is, a bond in which the

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Table IV. Summary of Townes-Dailey Analyses of ^{17}O NQR Results for Oxygen Singly Connected to Nitrogen

compd	rel efg components	sign of q_{zz}	p_π	$p_\sigma{}^0$(0% s)	p_σ(10% s)	p_σ(20% s)	π-bond order	C^a
nitrobenzenes	$\lvert q_{yy}\rvert > \lvert q_{zz}\rvert > \lvert q_{xx}\rvert$	+	1.492	1.254	1.171	1.068	0.57	−0.56
γ-picoline *N*-oxide	$\lvert q_{zz}\rvert > \lvert q_{yy}\rvert > \lvert q_{xx}\rvert$	−	1.836	1.172	1.079	0.964	0.18	−0.80
imidazolium nitrate	$\lvert q_{zz}\rvert > \lvert q_{yy}\rvert > \lvert q_{xx}\rvert$	−	1.700	1.249	1.165	1.061	0.33	−0.76

[a] Net charge on oxygen assuming 20% s character in σ bond.

electron pair that forms the σ interaction can be viewed as having originated with one of the bonding atoms, in this case nitrogen. The value for $p_\sigma{}^0$ should be about 1.0; p_y is assumed to be 2.0, because there is no π-bond interaction with pyridine in the plane of the molecule; p_π should be somewhat less than 2, depending on the extent of π-bond interaction. Thus the molecular z axis should be coincident with the Z axis of the EFG tensor, and q_{yy} should be greater than q_{xx}, as indicated in Table IV.

Analysis of the ^{17}O data for the nitrate group of imidazolium nitrate follows along the lines indicated for the aromatic nitro group. The π-bond order in the nitrate N-O bonds should be about 0.3, consistent with an oxygen p_π orbital population of about 1.7, as calculated for the axis assignment given in Table IV. However, when the data for oxygen in this case are interpreted, it should be kept in mind that the field gradient is likely to be perturbed by a hydrogen-bonding interaction of the oxygen with the imidazolium ion. Indeed, it is just this hydrogen-bonding interaction that makes it possible to observe this oxygen, because of the relatively short oxygen-proton distance.

In the compounds containing P-O or S-O bonds, the EFG tensor at the singly connected oxygen should have axial or near-axial symmetry, along the P-O or S-O bond axis. Both the p_x and p_y orbitals can enter into π-bond interaction with vacant orbitals on P or S. For this situation the Townes-Dailey analysis yields eq 3. From these expressions η can be written as in eq 4 from which it follows that

$$q_{zz}/q_{210} = -p_{\pi_x}/2 - p_{\pi_y}/2 + p_\sigma{}^0$$

$$q_{xx}/q_{210} = p_{\pi_x} - p_{\pi_y}/2 - p_\sigma{}^0/2 \qquad (3)$$

$$q_{yy}/q_{210} = p_{\pi_y} - p_{\pi_x}/2 - p_\sigma{}^0/2$$

$$\eta = (q_{210}/q_{zz})(3/2)(p_{\pi_x} - p_{\pi_y}) \qquad (4)$$

$$p_{\pi_x} = p_\sigma{}^0 - (q_{zz}/q_{210})(1 - \eta/3) \qquad (5)$$

$$p_{\pi_y} = p_\sigma{}^0 - (q_{zz}/q_{210})(1 + \eta/3) \qquad (6)$$

When η is small, $q_{zz}/q_{210} \approx p_\sigma{}^0 - p_\pi$, where p is the averaged population of the p_x and p_y orbitals. In general p_π is greater than $p_\sigma{}^0$; q_{zz} is negative, inasmuch as e^2Qq_{210}/h is positive.[3,14]

Because there are only two independently observable parameters of the EFG tensor, it is not possible to determine values for all three quantities, p_{π_x}, p_{π_y}, and $p_\sigma{}^0$. (When $\eta = 0$, e^2Qq_{zz} is the only independent parameter and there remain two unknowns, $p_\sigma{}^0$ and p_π.) Thus it is necessary to make an independent estimate of one of the quantities. For oxygen bound to carbon in carbonyl compounds, $p_\sigma{}^0$ is about 1.55.[3] As noted above, for oxygen singly bound to nitrogen in nitro compounds or nitrate, $p_\sigma{}^0$ is estimated as 1.25. It is reasonable to expect that $p_\sigma{}^0$ should vary monotonically with the electronegativity of the atom to which oxygen is bound. We assume a linear relationship with electronegativity. The theoretically derived electronegativities for the elements of interest, in appropriate hybridization states, are as follows:[16] carbon (sp^2), 2.75; sulfur (sp^3), 3.21; phosphorus (sp^3), 2.79; nitrogen (sp^2), 4.13. A linear interpolation yields $p_\sigma{}^0$ values of 1.54 for oxygen bonded to phosphorus and 1.45 for oxygen bound to sulfur. These values are only rough estimates, but the relative values of $p_\sigma{}^0$ among the four elements are certainly correct.

Table V. Estimated π- and σ-Bond Populations for Oxygen Bound to P or S^a

compd	p_{π_x}	p_{π_y}	$p_\sigma{}^0$ (0% s)	p_σ (15% s)	p_σ (25% s)	π-electron transfer
triphenyl phosphate	1.73	1.72	1.54	1.45	1.39	0.55
triphenylphosphine oxide	1.77	1.76	1.54	1.45	1.39	0.47
diphenyl sulfoxide	1.94	1.87	1.45	1.35	1.27	0.19
bis(*p*-chlorophenyl) sulfoxide	1.94	1.87	1.45	1.35	1.27	0.19
diphenyl sulfone	1.80	1.75	1.45	1.35	1.27	0.45
bis(*p*-chlorophenyl) sulfone	1.80	1.74	1.45	1.35	1.27	0.46

[a] Based on the Townes-Dailey Analysis.

Table VI. Calculated Quadrupole Coupling Constants and Asymmetry Parameters for Various π-Orbital Populations, for Oxygens Unicoordinated to Nitrogen^a

	p_π			
	2.0	1.8	1.6	1.4
q_{zz}/q_{210}	−0.75	−0.65	−0.55	−0.45
q_{xx}/q_{210}	0.375	0.175	−0.025	−0.225
q_{yy}/q_{210}	0.375	0.475	0.575	0.675
e^2Qq/h, MHz	−15.7	−13.6	12.0	14.1
η	0.0	0.46	0.91	0.33

[a] Assuming $p_\sigma{}^0 = 1.25$.

Using the values of $p_\sigma{}^0$ indicated above, one can then estimate values for p_{π_x} and p_{π_y}. We expect that the p_π orbitals will have a greater population than the σ orbital. The resultant estimates for p_{π_x} and p_{π_y} are given in Table V. The absence of π bonding would require p_x and p_y populations of 2. The total π-electron transfer is defined as $(4 - p_{\pi_x} - p_{\pi_y})$. This estimate is independent of the assumed fractional s character in the σ bond from oxygen to phosphorus or sulfur. Values of p_σ are listed in Tables IV and V for varying levels of assumed fractional s character.

Discussion

It is apparent from Table I that the N-O bonds of the nitro group vary insignificantly for different substituents in meta and para positions of nitrobenzene. The ^{17}O nuclear quadrupole coupling constants are all within 0.03 MHz of 13.12 MHz. A change of orbital population of one electron corresponds to a coupling constant change on the order of 20 MHz. Thus the variation of orbital populations on oxygen in the nitro compounds is no greater than 1×10^{-3} electrons. By contrast, the variation in ^{14}N EFG parameters in the same seies of compounds[17] suggests variations in orbital populations on the order of 2×10^{-2} electrons, at least an order of magnitude larger change. The reason for the insensitivity of the ^{17}O EFG parameters to substituent changes is under investigation.

It is noteworthy that our analysis leads to different orientations of the oxygen EFG principal axes in the nitrobenzenes as compared with picoline *N*-oxide and the nitrate ion, as indicated in Table IV. The difference is the result of differing p_π orbital populations. The situation is analogous to that encountered in the analysis of ^{17}O data for organic carbonyl groups.[3] To illustrate, consider the axis system illustrated in Figure 1, and assume $p_\sigma{}^0 = 1.25$ and $p_y = 2.0$. The values calculated for q_{zz}/q_{210}, q_{xx}/q_{210}, and q_{yy}/q_{210} are given in Table VI for various assumed values of p_π. As p_π decreases due to increasing extent of π bonding, e^2Qq/h decreases. When p_π reaches a value of about 1.65, η has increased to 1. At still lower values of p_π, the principal axis of the EFG tensor is

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aligned along the molecular y axis. This orientation of the EFG tensor is likely to obtain for all nitro and nitroso compounds; p_π must decrease to well below 1.4 before another change in the orientation of the tensor axis occurs.

The values assigned from Townes–Dailey analysis to the σ orbital population are dependent on the assumed fractional s character in the bond. Unfortunately, there is no set of independent experimental observations that serves to fix this quantity. (Hopefully it will be possible to employ ^{17}O scalar coupling constant data for this purpose when such data become available.) It is reasonable to assume, however, an amount of s character roughly comparable to that expected from simple hybridization arguments. Table IV lists values for the σ orbital population, p_σ, assuming 0%, 10%, and 20% s character. The largest of these seems the most reasonable estimate. For oxygen in the bonding situation depicted in Figure 1, the net charge on oxygen, C, is related to the population estimates as $C = 2 - \mathrm{p}_\pi - p_\sigma$. The values of C for an assumed 20% fractional s character are listed in the last column of Table IV.

The N–O π-bond order listed in Table IV is estimated by considering a simple valence bond picture of a double bond. We can assume that since oxygen is slightly more electronegative than nitrogen, the p_π orbital population for a full π bond would be slightly larger than 1.0, say 1.1. The p_π orbital population in the absence of a π bond would be 2.0. Then for a partial π bond of order X we can write eq 7. The π-bond orders calculated from

$$p_\pi = 1.1X + 2(1 - X) \tag{7}$$

use of this simple relationship are listed in Table IV. It is interesting that for the nitro groups the calculated π-bond order, 0.57, is not so far from the value 0.5 expected from simple valence bond arguments. The value of 0.33 for the nitrate oxygen is (no doubt fortuitously) equal to the naive expectation of a $^1/_3$ π-bond order.

The ^{17}O NQR results for picoline *N*-oxide are especially interesting because they provide the first experimental basis for a quantitative estimate of the π-bond character in the N–O bond. The estimated π-bond order of 0.18 for picoline *N*-oxide is consistent with various experimental evidences of some π bonding between oxygen and nitrogen,[18] in particular the relatively high N–O stretching frequencies[19] and molecular dipole moments[20] in various substituted pyridine *N*-oxides, and the N–O bond distance as deduced from electron diffraction[21] and microwave spectral[22] studies. An ab initio SCF calculation, with configuration interaction, of pyridine *N*-oxide was recently reported.[23] The computed EFG parameters for ^{17}O are not close to the observed experimental results; it is particularly distressing that the calculated asymmetry parameter, 0.809, is far from the observed value.

Like the N–O bond in picoline *N*-oxide, the bonds to oxygen in phosphine oxide, phosphate, sulfone, and sulfoxide compounds are also of the semipolar type.[24] The question of the extent of multiple bonding arises in all such bonding situations whenever the atom that "donates" the σ-bonding electrons has available an orbital of π symmetry that can act as acceptor. The P–O bond length of 1.43 Å in triphenyl phosphate[12] is substantially shorter than the bridging P–O bond lengths of 1.56 and 1.60 Å in two different forms of P_4O_{10},[25,26] suggesting substantial multiple bond character. A high bond order is reflected also in the high thermal stability of the P–O bond and its high stretching force constant. The presence of substantial π bonding is evident in the ^{17}O NQR data. When a choice of value was made for p_σ^0 on the basis of electronegativity difference between P and O, the p_{π_x} and p_{π_y} orbital populations follow directly from the observed EFG parameters via eq 5 and 6. Because there is charge transfer between P and O in both the π and σ bonds, it is not entirely clear what value of p_{π_x} and p_{π_y} should represent a full π bond of order 1 between P and O. Whatever the value employed however, it is evident that there is a substantial transfer of electrons from oxygen to phosphorus via the π orbitals in both triphenylphosphine oxide and triphenyl phosphate. The total π-electronic charge transfer in the phosphate is 0.55 e^-, and 0.47 e^- in triphenylphosphine oxide. These values are in the range calculated for H_3PO.[24,27] Thus, the NQR evidence is that π bonding between oxygen and phosphorus in triphenyl phosphate and triphenylphosphine oxide occurs to a similar, substantial extent in both compounds.

The π bonding between sulfur and oxygen in sulfones and sulfoxides is generally believed to be an important feature of the S–O bond.[24,28] The crystal structures of a few aryl sulfoxides are known,[29] the S–O bond length is in the range of 1.47–1.48 Å. These bond lengths are significantly shorter than the single bond length of 1.67 Å estimated from covalent radii, with a Schomaker–Stevenson correction.[30] The S–O bond lengths in sulfones[31] are consistently 0.05 Å shorter than those of the analogous sulfoxide. This shortening of the S–O bond length, ascribed to the influence of an electronegative group attached to sulfur, is further substantiated by the relatively short S–O bond length of 1.403 Å in F_4SO.[32] It is also interesting to note that the S–O length of a spirodiaryldialkoxysulfurane oxide is 1.439 Å,[33] which is closer to the S–O bond length in sulfones than in sulfoxides.

The orbital populations listed in Table V indicate that there is double-bond character between sulfur and oxygen in both sulfoxides and sulfones. However, the ^{17}O NQR data are remarkably different for the two types of compounds (Table II). The difference in the extent of π-electron transfer, 0.19 e^- for sulfoxide and 0.45 e^- for sulfones, seems rather large in light of the small observed difference in S–O bond distances in the two classes of compounds.

We believe that the major contribution to the nonzero values of η in the sulfoxides and sulfones is intramolecular in origin, rather than due to merely packing effects. Careful inspection of the structures of diphenylsulfone and diphenyl sulfoxide[29a,34] reveals that the distance between oxygen and the nearest hydrogens of the two phenyl rings is about 2.4 Å, some 0.3–0.5 Å less than the sum of van der Waals radii. This suggests that there might be a strong repulsion between the oxygen-centered and hydrogen-centered electronic charge distributions.

The data presented in this paper show that ^{17}O field gradient parameters are quite sensitive to the details of the electronic environment about oxygen. The wide range in observed values of e^2Qq_{ZZ}/h can be related in large measure to variations in the extent of π bonding. As more data accumulate, ^{17}O NQR spectroscopy should prove useful in functional group identification. In addition, for particular functional groups the field gradient parameters can be expected to vary with substituent effects and to be sensitive to other environmental effects such as hydrogen bonding and complex formation.

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