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Substituent Effects on ^{15}N and ^{17}O NMR Chemical Shifts in 4′-Substituted *trans-NNO*-Azoxybenzenes

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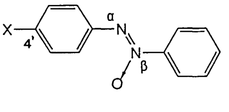
^{15}N and ^{17}O NMR spectra have been measured for a series of 4′-substituted *trans-NNO*-azoxybenzenes (AZOXY) and the obtained substituent chemical shift (SCS) values have been analyzed by means of the LSFE equation. Both the resonance and the polar contribution of substituents are important in determining the $^{15}N(\beta)$ SCS and the adjacent terminal ^{17}O SCS in the $-N_\alpha{=}N_\beta(O)-$ function of the AZOXY set. The resonance contributions of the AZOXY sets differ from those of the corresponding PYNO sets in view of a depressed pi-acceptor resonance contribution. That is, the resonance susceptibility ratio in the LSFE equation, ρ_π^+/ρ_π^-, varies from 1.4 (PYNO) to 2—4 (AZOXY) for both ^{15}N and ^{17}O SCS. The results are compared with the ^{13}C SCS of the corresponding positions in the relevant aromatic side-chain systems, and characterized in terms of repulsive pi-acceptor interaction between the substituents and the side-chain pi-electron systems. The importance of such dual resonance susceptibility has been shown for understanding characteristic features of the ^{15}N and the adjacent ^{17}O SCS.

Azoxybenzenes (AZOXY) have a $-N_\alpha{=}N_\beta(O)-$ function in the aromatic side-chain pi-electron system which involves a characteristic N → O dative bond. Although much attention has been attracted to this class of compounds,[1] the reactivities or physicochemical properties of the compositive atoms in the NNO function have been less studied than those in the corresponding pyridine 1-oxides (PYNO), especially with systematic and quantitative fashions.[2–4] To know the electronic properties of nitrogen and oxygen atoms incorporated with the AZOXY pi-electron system, ^{15}N and ^{17}O NMR approaches[5–7] were conducted several 4′-substituted *trans-NNO*-azoxybenzenes, each carrying an oxygen atom in the N_β position of the $-N_\alpha{=}N_\beta-$ double bond.



Applications or applicabilities of the LSFE equation (Eq. 1) to the substituent effects on reactivity data, especially on NMR substituent chemical shift (SCS) data, have been demonstrated in our several earlier papers.[8–12]

$$\mathrm{SCS} = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \rho_\pi^-\sigma_\pi^- \qquad (1)$$

Here, the LSFE substituent parameters are defined as follows:

$$\sigma_i = 0.74\ \sigma_I$$
$$\sigma_\pi^+ = 0.42\ \Delta\bar{\sigma}_R^+$$
$$\sigma_\pi^- = 0.73\ \Delta\bar{\sigma}_R^-$$
$$\sigma^0 = \sigma_i + \sigma_\pi^+ + \sigma_\pi^-$$

Since the parameters of σ_i, σ_π^+, and σ_π^- are dependent solely on electronic natures of substituents and independent of aromatic positions to which substituents are attached, the LSFE treatment must be a powerful tool for understanding general substituent electronic effects, beyond benzene systems, of fused aromatic, heteroaromatic, or aromatic side-chain systems. In this paper, we report the ^{15}N and ^{17}O NMR SCS data and analyses of 4′-substituted *trans-NNO*-azoxybenzenes in DMSO. The results are compared with those of the corresponding PYNO system[11] and other relevant aromatic side-chain systems.[7] The validity of the LSFE equation (Eq. 1) to the multinuclear SCS systems is presented.

Experimental

Materials. 4′-MeO-, 4′-Me-, 4′-Cl-substituted azoxybenzenes were prepared from condensation of nitrobenzene with the corresponding 4-substituted phenyliminodimagnesium reagent by using the previously reported procedure.[4] 4′-CF_3, 4′-CN, and 4′-NO_2 derivatives were obtained by the reaction sequence of (1) condensation of 4-nitroaniline with nitrosobenzene, (2) oxidation with *m*-chloroperbenzoic acid, and (3) isomerization with CrO_3 in CH_3COOH.[2,13] 4′-$COCH_3$ derivative was obtained by oxidation of 4′-C_2H_5 one. The unsubstituted one was taken from a commercial sample. All were purified several times by recrystallization from appropriate solvent, e.g., petroleum ether or aqueous ethanol. Melting points[2–4,13,14] of 4′-substituted *trans-NNO*-azoxybenzenes utilized were as follows [X, mp (°C)]: 4′-MeO, 70.8—71.2; 4′-Me, 48.0—48.1; H, 32.5—32.8; 4′-Cl, 66.1—66.3; 4′-CF_3, 99.0—99.7; 4′-$COCH_3$, 121.0—121.5; 4′-CN, 114.0—115.0; 4′-NO_2, 155.0—155.3.

NMR Measurements. NMR spectra were measured on a Bruker AM360 spectrometer at 48.84 MHz at 80 °C for ^{17}O NMR[11,15,16] and 36.50 MHz at room temperature for ^{15}N NMR,[11] with a 10 mm ϕ tube for solutions of 200—300 mg in DMSO (2 mL). Typical experimental conditions for ^{17}O NMR measurements were acquisition time of 15 ms, 1k data points, 33 kHz spectral width, 1×10^6 scans, 4k data for processing (3k zero-filling). ^{17}O chemical shift values were determined from the ^{17}O signal of DMSO as an internal reference. In some cases, Burg's maximum entropy method (MEM)[17] was utilized for FID data processing instead of FFT to get relatively sharp ^{17}O signals. Data records have been acquired with the above NMR spectrometer and transferred to FACOM S3500 superminicomputer, being a host computer in our TASMAC system, ISIR, Osaka Univ.[18] The obtained SCS values usually have an estimated error of ±2 ppm, except for 4′-CF_3 and 4′-$COCH_3$ (±4 ppm).

On the other hand, typical experimental conditions for ^{15}N INEPT measurements were acquisition time of 2.4 s, spectral width of 3.4 kHz, 16k data points, and $\Delta_t=0.25/(J_{NH})=0.122$ s. ^{15}N chemical shift values were determined with external CH_3NO_2 in a capillary tube. The obtained SCS values have an estimated error of ±0.1 ppm.

Pi-Electron Density Calculations. Calculations of geometries for various 4′-substituted *trans-NNO*-azoxybenzenes were carried out on the FACOM S3500 superminicomputer (ANCHOR in TASMAC System)[18] by using MNDO molecular orbital methods.[19,20] The geometries were obtained from the standard DFP optimization procedures. Except where noted otherwise, all geometrical variables were allowed to optimize by using default values. For ab initio MO calculations,[21,22] the MNDO optimized geometries were employed subsequently in single point calculations of Gaussian 80 program with the STO-3G basis set.[23] The corresponding O(2p$_Y$) and N(2p$_Y$) values of gross orbital charges in Mulliken population analysis were utilized for calculations of Δq_π(O) and Δq_π(N) values.

X-Ray Structure Analysis. Crystals for X-ray analysis of 4′-Cl derivative (AZOXY) were obtained by slow evaporation from a solution in hexane at room temperature. X-Ray structure determination was performed with the same method as that for the other compounds solved by our groups on the TASMAC.[25] The obtained crystal structure shows that the two phenyl rings are coplanar each other.[24] The crystal data of *trans*-4′-chloro-*NNO*-azoxybenzene, $C_{12}H_9N_2O_1Cl_1$, are as follows: triclinic, space group $P\bar{1}$, $a=11.205(4)$, $b=7.744(2)$, $c=6.664(2)$ Å, $\alpha=74.46(3)$, $\beta=98.76(3)$, $\gamma=97.88(3)°$, $V=547.8$ Å^3, $Z=2$, $\rho_{calcd}=1.411$ g cm^{-3}, $R=0.066$ for unique 1203 reflections (Mo $K\alpha$, $\lambda=0.71069$ Å). Atomic coordinates, bond lengths and angles, thermal parameters, and F_o-F_c tables have been deposited as Document No. 8914 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The ^{15}N and ^{17}O NMR substituent chemical shift (SCS) values for the AZOXY system as well as those for the corresponding PYNO system[11,15] are summarized in Table 1. Assignment of the two nitrogen peaks (^{15}N(α) and ^{15}N(β)) in the AZOXY set was carried out from a combined application of (1) literature data of ^{15}N chemical shift on the basis of a ^{15}N labelled sample,[26] (2) broadening of ^{15}N INEPT peak, and (3) comparison of proton-nondecoupled ^{15}N spectral pattern with the calculated one by using $^5J_{NH}=1.5$ Hz.

^{15}N(β) and ^{17}O SCS are shifted downfield by electron acceptor substituents (Hammett σ scale), but ^{15}N(α) SCS is shifted upfield in the AZOXY system.

Neither the ^{15}N(β) SCS nor ^{17}O SCS in the AZOXY set provides excellent overall linearities with the corresponding ^{15}N or ^{17}O SCS in the PYNO set:[11] i.e., correlation coefficient (r) for a ^{17}O–^{17}O plot between the AZOXY and the PYNO sets is 0.989 (n=7) and that for a ^{15}N–^{15}N plot is 0.987 (n=7). This suggests certain difference of substituent effects on the two types of the N → O function such as an aromatic N → O and an aromatic side-chain N → O. On the other hand, the ^{15}N(β) SCS in the AZOXY set shows much better linear relationship, (including pi-donor to pi-acceptor substituents), with the ^{13}C(β) SCS in the 4-substituted β-nitrostyrene set,[26]

$$(^{15}\text{N}(\beta)\ \text{AZOXY SCS}) = 2.48(^{13}\text{C}(\beta)\ \beta\text{-NO}_2\text{-STYRENE SCS}) - 0.53 \quad (r = 0.996,\ n = 6),$$

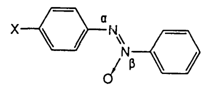
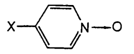
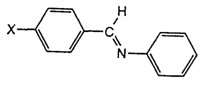
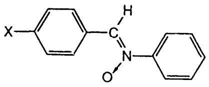
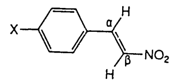
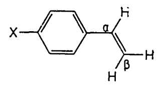
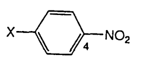
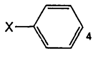
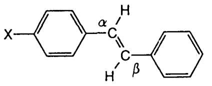
compared with that in the 4-substituted styrene set (r=0.978 (n=7)).[27]

Table 1. NMR SCS in DMSO and Relative Pi-Electron Density of 4′-Substituted *trans-NNO*-Azoxybenzenes[a]

	AZOXY					PYNO[b]	
Subst	^{17}O SCS /ppm 80 °C	$10^3\Delta q_\pi$(O) /eu (STO-3G)[h]	^{15}N(β) SCS /ppm r.t.	$10^3\Delta q_\pi(\text{N})_\beta$ /eu (STO-3G)[h]	^{15}N(α) SCS /ppm r.t.	^{17}O SCS /ppm 80 °C	^{15}N SCS /ppm r.t.
4′-CH_3O	−11	−9	−6.7	−3	−2.4	−33	−18.0
4′-CH_3	−5	−3	−2.4	−1	−0.7	−13	−6.6
H	0[c]	0[i]	0.0[d]	0[j]	0.0[e]	0	0.0
4′-F		−1		0			
4′-Cl	2	(9)	0.8	(6)	−3.2	6	−2.5
4′-CF_3	8[f]		5.0		−2.4		
4′-$COCH_3$	8[f]	8[g]	4.1	3[g]	−1.1	39	8.7
4′-CN	15	14	5.5	8	−2.9	52	9.2
4′-NO_2	16	22	6.5	9	−3.5	65	13.3

a) Negative sign indicates a high field shift in NMR SCS and an increase in pi-electron density. b) Ref. 11. c) 444 ppm from solvent DMSO. d) −57.3 ppm from external CH_3NO_2. e) −52.1 ppm from external CH_3NO_2. f) an estimated error is ±4 ppm. g) Partially optimized. h) Refs. 19, 20—23. i) q_π(O)=1.442. j) $q_\pi(\text{N})_\beta$=1.255.

Table 2. LSFE Results for ^{15}N, ^{17}O, ^{13}C SCS of Azoxybenzene and Related Systems[a,b]
$\mathrm{SCS}=\rho_i\sigma_i+\rho_\pi^+\sigma_\pi^+ +\rho_\pi^-\sigma_\pi^-$

No.	System	Solvent	Probe	ρ_i	ρ_π^+	ρ_π^-	ρ_π^+/ρ_π^-	Note[c]	Ref.
1:		DMSO DMSO DMSO	^{17}O ^{15}N(β) ^{15}N(α)	20 9 (ca. −7)	50 31 (ca. 3)	22 8 (ca. 2)	ca. 2 3.9 	0.985[8] 0.995[8] 0.949[8]	Present Present Present
2:		DMSO DMSO	^{17}O ^{15}N	57 5	150 50	110 37	1.4 1.4	See lit. [10] See lit. [10]	11 11
3:		DMSO	^{15}N	10	36	ca. 19	ca. 1.8	0.995[6]	28a
4:		CDCl3	^{15}N	8	28	17	1.7	0.997[9]	28b
5:		DMSO	^{13}C(β)	3.4	11.4	3.9	2.9	0.9985[11]	27a
6:		DMSO	^{13}C(β)	4.9	10.6	9.3	1.1	0.9945[12]	27b
7:		DMSO	^{13}C(4)	0.6	22.6	8.5	2.7	0.998[20]	9b
8:		DMSO	^{13}C(4)	2.4	21.7	19.4	1.1	0.992[24]	9a
9:		CDCl3	^{13}C(β)	3.9	8.4	8.8	0.9	0.9968[13]	27d

a) Substituent parameters utilized are taken from Ref. 10c. b) Parentheses show values based on a correlation coefficient less than 0.95 in nonconjugative positions. c) Correlation coefficient [number of points].

The LSFE equation (Eq. 1)[8—12] was used to separate the obtained ^{15}N and ^{17}O NMR SCS data into polar and resonance (pi-electronic) contributions. Results of the correlation analysis are summarized in Table 2, together with those for the corresponding PYNO,[11] benzene,[9a] 4-nitrobenzene,[9b] *N*-(phenylmethylene)benzenamine(BA),[28a] α,*N*-diphenyl nitrone(NITRONE),[28b] styrene,[27b] β-nitrostyrene,[27a] and stilbene[27d] systems in DMSO solution. Generally, ^{15}N SCS is 2—3 times more sensitive than the corresponding ^{13}C SCS:[7] comparison of the system Nos. **1**, **3**, **4** with **9** (Table 2).

The results at the conjugated positions in Table 2 show that substituent effects are indicative of variously varying resonance susceptibility ratio (the relative contribution of pi-donor resonance to pi-acceptor resonance, ρ_π^+/ρ_π^-) at different systems and different probe atoms. The important feature of the AZOXY set is a decreasing contribution of pi-acceptor resonance (ρ_π^- value), especially compared with that of the corresponding PYNO set. Thus, the ρ_π^+/ρ_π^- value increases from 1.4 (PYNO **2**) to 3.9, ca. 2 (AZOXY **1**) for ^{15}N(β), ^{17}O SCS, respectively.

In the case of ^{13}C NMR SCS, when a NO_2 group is a fixed substituent attached directly to the probe carbon atom in an aromatic or aromatic side-chain system, the ρ_π^+/ρ_π^- value increases substantially from 1.1 (^{13}C(4) in **8** or ^{13}C(β) in **6**) to 2.8 (^{13}C(4) in **7** or ^{13}C(β) in **5**). This phenomenon has been rationalized in terms of depressed resonance contribution from pi-acceptor substituents which arises from the repulsive interaction at the probe atom with the positive charge induced by the directly bonded NO_2 group.[9b] The introduction of a phenyl group in the β position of the styrene system does not provide a large change in the ρ_π^+/ρ_π^- magnitude; that is, from 1.1 (^{13}C(β) in **6**) to 0.9 (^{13}C(β) in **9**).

In the case of ^{15}N(β) SCS of the aromatic side-chain systems, the relative contribution of pi-donor resonance effect of substituents to polar effect (ρ_π^+/ρ_i) is nearly equal for the three AZOXY, BA, NITRONE systems (3.4 for **1**, 3.6 for **3**, 3.5 for **4**), and is a somewhat larger value than that for the corresponding styrene systems (2.2 for **6**, 2.2 for **9**). This observation reflects an enhanced pi-donor resonance from substituents to the N_β nitrogen atom incorporated in the functional group such as $-N=N_\beta(O)-$, $-CH=N_\beta-$, or $-CH=N_\beta(O)-$. This effect is ascribed to the greater pi-acceptor character of these functional groups due to the electronegative nitrogen atom. Whilst the relative contribution of pi-acceptor resonance effect of substituents to polar one (ρ_π^-/ρ_i) is almost equal for the NITRONE, BA (2.1 for **4**, ca. 2 for **3**) and styrene, stilbene systems (1.9 for **6**, 2.2 for **9**), this ratio value for the AZOXY system is characteristically small (0.9 for **1**), and close to that for the β-nitrostyrene system (1.1 for **5**). One possible interpretation is this is due to compensation by pi-electrons of the adjacent oxygen as expected by a canonical structure. If this is true, the ρ_π^-/ρ_i value for the ^{17}O SCS should be enhanced. However, this effect is not enhanced (see later). Fortunately, we can use numerical values of $\Delta\bar{\sigma}_R^-$ parameter in the Yukawa-Tsuno equation, as a measure of the relative pi-acceptor resonance ability of the whole group: $\Delta\bar{\sigma}_R^-$ is 0.31 for $-N=N-C_6H_5$, ca. 0.37 for $-CH=CH-NO_2$, 0.14 for $-CH=N-C_6H_5$.[8b)] Since a larger $\Delta\bar{\sigma}_R^-$ value may be expected for $-N=N(O)-C_6H_5$, the depressed effect is due to repulsive interaction between pi-acceptor substituents and the pi-acceptor functional group. Then, the above donor–acceptor two types of resonance contribution are combined in the magnitude of ρ_π^+/ρ_π^-, resulting in 1.0 (styrene, stilbene), 1.7 (BA, NITRONE), and 3.9 (AZOXY).

On the other hand, the ^{17}O SCS is less reliable than the ^{15}N SCS because of the substantial broadenings of ^{17}O signals. The ρ_π^+/ρ_i value for the AZOXY is nevertheless obtained to be approximately the same as that for the PYNO set (ca. 3 for **1**, 2.6 for **2**). The ρ_π^-/ρ_i value for the AZOXY is approximately a half of that for the PYNO set (ca. 1 for **1**, 1.9 for **2**). Again, the depressed pi-acceptor resonance is supported. Consequently, the identical results of such depressed pi-acceptor resonance for both the ^{15}N(β) SCS and the adjacent ^{17}O SCS indicate that there are only weak pi-acceptor resonance interactions between the substituents and the side-chain NNO pi-system in the AZOXY set.

In the Taft's DSP treatment,[7,29)] such a change of the relative resonance contribution (ρ_π^+/ρ_π^-) might be replaced and masked by the change of one of four resonance parameters, (σ^0, σ_R(BA), σ_R^+, σ_R^-).[27c,e)]

$$(^{15}\text{N}(\beta)\ \text{AZOXY SCS}) = 7.8\sigma_I + 13.6\sigma_R(\text{BA})$$
$$(r = 0.994, n = 8)$$

$$(^{17}\text{O AZOXY SCS}) = 20\sigma_I + 25\sigma_R(\text{BA})$$
$$(r = 0.991, n = 8)$$

$$(^{15}\text{N PYNO SCS}) = 12.6\sigma_I + 34.5\sigma_R(\text{BA})$$
$$(r = 0.992, n = 9)$$

$$(^{17}\text{O PYNO SCS}) = 65\sigma_I + 117\sigma_R^0$$
$$(r = 0.996, n = 9)$$

By contrast, the LSFE analysis is unsuccessful to ^{15}N(α) SCS in the nonconjugated position of the $-N_\alpha=N(O)-$ function, as shown typically by correlation coefficient data (r<0.95) in Table 2. Reverse and relatively large polar effect might be noted. This type of reverse substituent effects has been generally observed for ^{15}N and ^{13}C SCS of certain aromatic side-chain systems, as mentioned in the literature.[5c,7,30,31)]

ab initio MO calculations at STO-3G level have already known to be useful, for example, for ^{13}C, ^{15}N, ^{19}F, and other NMR SCS.[5c,7,21,32)] The ^{17}O SCS gives a satisfactory correlation with Δq_π(O), relative pi-electron density at oxygen, for a combined data set of the AZOXY (4-substituents, n=6) and the PYNO (3- and 4-substituents, n=11) sets. The slope is 990 ppm/pi-electron; r=0.987, n=17 (Fig. 1). This SCR (shift-charge ratio) value is a somewhat smaller one than that for the other oxygen systems reported.[5c,7,29,32b)] The ^{15}N(β) SCS vs Δq_π(N) plot for the same combined data set of the AZOXY (4-substituents, n=6) and the PYNO (3- and 4-substituents, n=11) shows a slightly scattering pattern; (SCR=ca. 750 ppm/pi-electron, r=0.88, n=17). The primary cause of such a pattern comes from the deviations of 3-substituted PYNO.

The obtained ^{15}N and ^{17}O SCS, coupled with the reported ^{13}C SCS of the relevant systems in the literature,[33)] provide an overall pattern of the substituent effect at various probe atoms incorporated with the AZOXY pi-electron system, as illustrated in a Chart. At a first glance, branching terminal ^{17}O SCS seems to be parallel to adjacent ^{15}N(β) SCS in the AZOXY set, since both SCS data give normal substituent effects (NSE). At a more advanced level, the nitrogen and the adjacent oxygen SCS of the side-chain N → O in the AZOXY system have a different

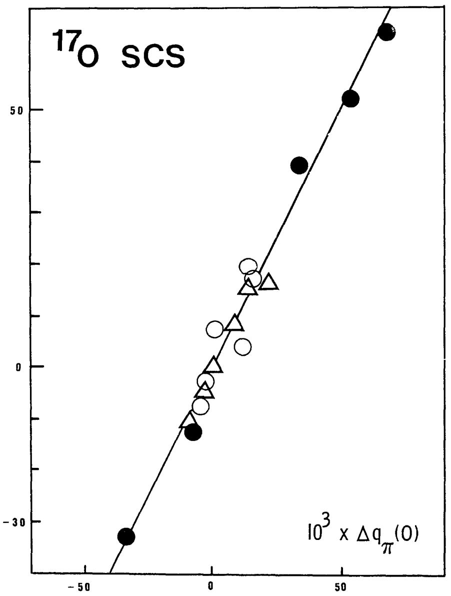


Fig. 1. A plot of observed ^{17}O NMR SCS (ppm) against calculated pi-electron density at oxygen (eu) of the AZOXY and PYNO sets: ○ 3-X-PYNO, ● 4-X-PYNO, △ 4-X-AZOXY.

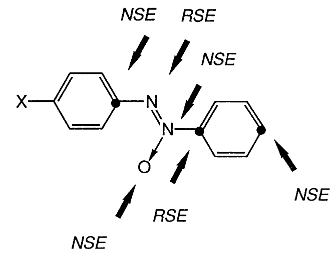


Chart 1. A pattern of observed and calculated substituent effects (SE) in the AZOXY set. NSE: (Normal SE): RSE: (Reverse SE).

resonance susceptibility ratio (ρ_π^+/ρ_π^-) from those of the aromatic ring $N \rightarrow O$ in the PYNO one,[11] mainly due to more decreasing contribution of pi-acceptor resonance in the AZOXY set. This type of analysis has been performed by using the LSFE treatment which allows dual types of resonance susceptibility.

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