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Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Carbodiimides[1]

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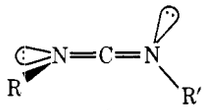
High-resolution, 18.25-MHz nitrogen-15 NMR spectra of several carbodiimides (1) have been obtained at the natural-abundance level. The high-field positions of the ^{15}N resonances of these substances are discussed in terms of two different shielding mechanisms. Solvent influences on the ^{15}N and ^{13}C chemical shifts of carbodiimides are small. Both the ^{13}C and ^{15}N spectra of 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride indicate that at least four different structural isomers are present in dimethyl sulfoxide solution at room temperature. Information about the dimerization of carbodiimides in the presence of alkylating agents has been obtained from ^{15}N and ^{13}C NMR.

Carbodiimides have attracted much attention because of their importance as versatile reagents in organic and biochemical synthesis.[2] That these substances have dissymmetric allene-like structures (1) is well established.[3] Optical isomerism is possible[4] but resolutions have not been achieved because of the low free-energy barrier to racemization (thus $\Delta G^{\ddagger}$ for diisopropylcarbodiimide is only 6.7 kcal/mol).[5] A recent ^{13}C NMR study[6] of 1 has demonstrated an unusually high-field shift (~140 ppm) for the sp-hybridized carbon of carbodiimides.



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We now report natural-abundance ^{15}N NMR studies of the carbodiimides **2–6** in a variety of neutral, basic, and acidic solvents at room temperature.

$(CH_3)_2CHN{=}C{=}NCH(CH_3)_2$ **2**

$C_6H_{11}N{=}C{=}NC_6H_{11}$ **3**

$(CH_3)_2CHN{=}C{=}NC(CH_3)_3$ **4**

$(CH_3)_2CHN{=}C{=}NC_6H_5$ **5**

$CH_3CH_2N{=}C{=}NCH_2CH_2CH_2N(CH_3)_2$ **6**

Experimental Section

Compounds **4**,[7] **5**,[7] and **6**[8] were prepared as previously described. Compounds **2**, **3**, **7**, **8**, and **10** were obtained from Aldrich and used without further purification. Reagent-grade solvents were employed in the present study.

The natural abundance ^{15}N NMR spectra were obtained at 18.25 MHz with a Bruker WH-180 pulse spectrometer which has been described in detail elsewhere.[9] A 25-mm o.d. spinning sample tube containing about 25 mL of sample was used. Useful spectra could usually be obtained with accumulation times of 3–4 h, a 45° pulse angle, 8K data points, 7000-Hz spectrum width, and a pulse interval of 30 s. A 5-mm concentric tube containing a 1 M solution of 98% ^{15}N-enriched nitric acid in D_2O provided both the external reference standard and the field-frequency lock. The protons were decoupled at a power of 4 W by a gating technique.[10] The sample temperatures were about 30 °C. Nitrogen-15 chemical shifts are reported in ppm upfield from $H^{15}NO_3$ with a precision of about ±0.1 ppm.

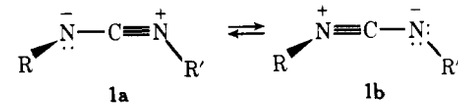
The natural-abundance ^{13}C NMR spectra were obtained at 25.2 MHz with a Varian XL-100-15 NMR spectrometer. Protons were noise decoupled and the spectra are the Fourier transforms of the sums of about 1000 free-induction decays obtained with a 30° pulse angle, 8K data points, and 5000-Hz spectrum width.

Results and Discussion

Nitrogen-15 NMR Spectra. Nitrogen-15 chemical shifts of several carbodiimides and related compounds are shown in Table I. Symmetrically substituted carbodiimides (**2** and **3**), as expected, exhibit only one ^{15}N resonance.[5] Unsymmetrical carbodiimides (**4** and **5**) show two distinct resonances which can be assigned by comparison with the ^{15}N chemical shift of **2**. The dimethylaminocarbodiimide (**6**) exhibits three resonances, one of which appears at a very much higher field than the others and therefore is attributed to the dimethylamino group. The remaining two signals of **6** are separated from one another by 3 ppm and could not be assigned unambiguously.

The ^{15}N chemical shifts of nitrogens of carbodiimides, like their ^{13}C carbons, are at quite high fields. In this respect, the nitrogens of carbodiimides are very different from imines ($R_1R_2C{=}N{-}R$) which have their ^{15}N resonances at *ca.* +50 ppm,[11] almost 220 ppm farther downfield. The high-field positions of the carbodiimide nitrogens, however, are paralleled by the nitrogen shifts of isocyanates (RN=C=O) and isothiocyanates (RN=C=S) (see Table I).

One possible difference between imines and carbodiimides could be through contributions of polar resonance structures such as **1a** and **1b** for the diimides. Such resonance would



1a **1b**

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Table I. Nitrogen-15 Resonances[a] in Carbodiimides and Related Compounds

compd	registry no.	solvent	concn[b]	^{15}N shifts
2	693-13-0	cyclohexane	20	271.7
		triethylamine	20	271.2
		dimethyl sulfate	20	271.0
		methyl iodide	20	270.9
		none	100	270.9
		chloroform	20	270.4
		dimethyl sulfoxide	20	270.0
		trifluoroethanol	20	267.8
		trifluoroethanol[c]	20	267.7 (carbodiimide)
				245.9 (pseudourea)
3	538-75-0	methyl iodide	10	275.0
		dimethyl sulfate	10	274.9
		chloroform	10	274.5
4	55546-43-5	cyclohexane	20	269.6 (*i*-PrN=)
				261.4 (*t*-BuN=)
5	14041-89-5	dimethyl sulfoxide	20	277.5 (C_6H_5N=)
				264.6 (*i*-PrN=)
6	1892-57-5	none	100	352.9 (-$N(CH_3)_2$)
				291.0
				288.2
7	103-71-9	none	100	327.5
8	103-72-0	none	100	266.9
$CH_3C{\equiv}N$	75-05-8	none	100	130.2
		CF_3COOH	10	146.6
$CH_3C{\equiv}N^+H$[d]		90% H_2SO_4	10	246.0
		FSO_3H–SbF_5–SO_2		239.4[d]

[a] In parts per million *upfield* from external nitric acid (1 M 98% ^{15}N-enriched nitric acid in D_2O). [b] Percent v:v. [c] Solution warmed at 80 °C for a few hours. [d] See ref 12.

certainly make the interconversion of the chiral forms of diimide more facile because, as written in **1a** and **1b**, they are not in the optimum linear geometrical configuration.

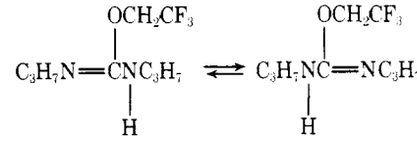
If such resonance forms can be considered to contribute, there are analogies that can be cited which can help rationalize the unusual upfield shifts. Thus, the ^{15}N chemical shift of acetonitrile is about 80 ppm upfield from that of an imine group, and protonation of acetonitrile at the nitrogen atom with formation of $CH_3C{\equiv}NH^+$ results in an upfield shift of about 120 ppm (see Table I).[12] It seems likely, however, that the most important difference between imine and diimide nitrogens could be the difference in n → π^* transition energies which are especially important in determining the paramagnetic shieldings.[13] To have increased shielding of the nitrogens and carbons of carbodiimides, the n → π^* (or other appropriate transition energies) must be greater than for imines. These differences in chemical shifts are much too large to be accounted for on the basis of purely diamagnetic effects.

Resonance structures analogous to **1a** and **1b** can also be written for isocyanates and isothiocyanates,[14] and it may be that the same considerations account for the high-field ^{15}N resonances of these compounds and those of the carbodiimides. The ^{15}N chemical shift of phenyl isocyanate (**7**) is about 70 ppm at higher field compared to that of phenyl isothiocyanate (**8**) (Table I). This rather large difference could be due to inefficient overlap of the p orbitals of carbon and sulfur, or else a lower electronic excitation energy for isothiocyanates as compared to isocyanates.

$C_6H_5N{=}C{=}O$ $C_6H_5N{=}C{=}S$

7 **8**

Highly polar solvents such as dimethyl sulfoxide cause a small, but distinct, downfield changes in the ^{15}N chemical shift of diisopropylcarbodiimide (**2**) (Table I). Hydrogen-bonding solvents such as chloroform and 2,2,2-trifluoroethanol (TFE) also induce small (ca. 2–4 ppm) downfield shifts and this could be quite significant in rationalizing the shifts of carbodiimides relative to imines, because hydrogen-bonding solvents with imines produce *upfield* shifts.[11] When a solution of **2** in trifluoroethanol is warmed at 80 °C for a few hours, the ^{15}N spectrum shows a new resonance at 245.9 ppm which is attributed to the pseudourea **9.** The nitrogens of **9** will only appear to be equivalent if proton exchange (**9a** ⇌ **9b**) occurs rapidly in trifluoroethanol at room temperature.



9a **9b**

Carbon-13 NMR Spectra. Carbon-13 chemical shifts of carbodiimides **2–6** are given in Table II. Assignments not previously reported were made with the help of gated and off-resonance proton-decoupling experiments. Three-bond carbon–hydrogen coupling constants were used to differentiate between the two quaternary carbon atoms in *N*-isopropyl-*N'*-phenylcarbodiimide (**5**). The proton-coupled carbon-13 NMR spectrum of **5** exhibits a 1:1 doublet ($^3J_{C-H}$ = 5.5 Hz) and a 1:2:1 triplet ($^3J_{C-H}$ = 8.5 Hz) for the two resonances at 136.1 and 141.0 ppm, respectively. The doublet at 136.1 ppm is assigned to the sp ^{13}C of the carbodiimide, which is spin–spin coupled to the methine proton of the isopropyl group. The triplet centered at 141.0 ppm is attributed to C1 of the phenyl group and is the result of coupling to the two protons on C3 and C5 ring carbons.

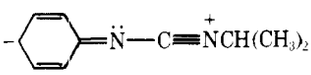
Unlike the ^{15}N chemical shifts of dialkylcarbodiimides which show substantial variations with the nature of the alkyl groups, the position of the sp ^{13}C of the carbodiimide moiety is almost insensitive to changes in the alkyl groups. In all dialkylcarbodiimides studied here, the sp ^{13}C appears at 140 ± 1 ppm. The sp ^{13}C of isopropylphenylcarbodiimide (**5**), however, is at a slightly higher field. The ^{13}C chemical shifts (Table II) indicate that the C2, C4, and C6 of the phenyl ring of **5** have electron densities significantly in excess of those for the carbon atoms of benzene itself (δ 128.5).[15] This enhanced charge

Table II. Carbon-13 Resonances[a] in Carbodiimides

compd	solvent	sp ^{13}C	other ^{13}C's
2	dimethyl sulfoxide	139.5	48.6 (CH), 25.7 (CH_3)
	chloroform[b]	140.2	49.0 (CH), 24.8 (CH_3)
	trifluoroethanol	142.5	50.4 (CH), 24.6 (CH_3)
3	dimethyl sulfoxide	139.1	55.1 (CH), 35.0 (C2, 6), 25.4 (C4), 24.4 (C3, 5)
	chloroform[b]	139.9	55.8 (CH), 35.0 (C2, 6), 25.5 (C4), 24.8 (C3, 5)
4	dimethyl sulfoxide	138.9	54.3 (C), 48.2 (CH), 31.1 $(CH_3)_3$, 24.5 $(CH_3)_2$
5	dimethyl sulfoxide	136.1	141.0 (C1), 129.6 (C3, 5), 124.7 (C4), 122.4 (C2, 6), 49.9 (CH)
6	dimethyl sulfoxide	140.0	56.3 (CH_2N), 45.2 (CH_3N), 44.0, 40.8 (CH_2N=), 29.0 (-CH_2-), 16.6 (CH_3)
	chloroform	140.6	56.9 (CH_2N), 45.6 (CH_3N), 44.8, 41.5 (CH_2N=), 29.5 (-CH_2-), 16.8 (CH_3)

[a] In parts per million downfield from internal tetramethylsilane. [b] From ref 6.

density could, in principle, arise from delocalization of the electron density into the ring in accord with resonance structure **10**, although the normal geometry of carbodiimides



10

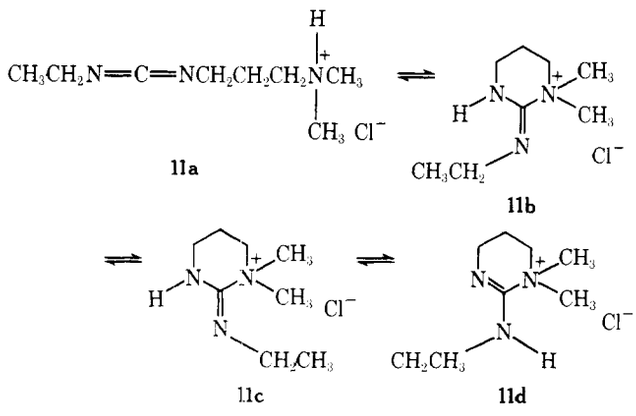
would not appear to allow for very important contributions of **10**, at least as far as the nitrogen carrying the isopropyl group is concerned.

Solvent changes have little effect on the ^{13}C chemical shifts of diisopropylcarbodiimide, and this is in accord with low basicity of the carbodiimide group as well as the ^{15}N chemical shifts previously discussed.

Water-Soluble Carbodiimides. The ureas and acylureas, formed as by-products in carbodiimide procedure for the amide bond formation, frequently have solubility properties similar to the peptides, rendering separation of the products difficult. To overcome this, Sheehan and Hlvaka[16] introduced water-soluble carbodiimides in 1956, because by-products of peptide syntheses with such carbodiimides are easily removed by washing with water.[17] One of the more frequently used water-soluble carbodiimide is 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (**11**).[17a] The infrared spectrum of **11** was found to have bands characteristic of -N=C=N-, NH, and -C=N- groups and interpreted in terms of the structural isomers **11a–d** (although no explicit mention was made of the two stereoisomers **11b** and **11c**).

The ^{13}C NMR spectrum of **11** in dimethyl sulfoxide shows at least 22 resonances at room temperature. Considering the possibility of coincidences and the presence of only seven different carbon atoms in the parent carbodiimide, it is reasonable to agree that there are at least four different isomers present which are interconverted slowly with respect to possible tautomeric and geometrical isomerizations[18] on the NMR time scale in dimethyl sulfoxide at room temperature.

The methyl-carbon resonances of the ethyl groups in the



11a **11b** **11c** **11d**

Table III. Carbon-13 and Nitrogen-15 Resonances[a] of **11**

carbon-13[b]	13.5, 15.6, 16.5, 17.3 ($^{13}CH_3C$); 25.2, 25.9 ($C^{13}CH_2C$); 33.9, 36.3, 36.5 ($^{13}CH_2N$=); 40.6, 40.9 (not assigned); 42.0, 42.3, 43.3 ($^{13}CH_3N$); 51.7, 52.9, 54.6, 60.4, 62.4 ($^{13}CH_2N$ or $^{13}CH_2N^+$); 141.2 (-N=C=N-); 147.7, 158.3 (^{13}C=N)
nitrogen-15[c]	164.6, 183.5 (^{15}N=C); 286.3, 307.9, 313.2 (^{15}N); 288.6, 291.9, 294.1, 302.3 (^{15}NH, $^1J_{N-H}$ = 88 Hz)

[a] In dimethyl-d_6 sulfoxide at room temperature. [b] In parts per million *downfield* from internal tetramethylsilane. [c] In parts per million *upfield* from external nitric acid (1 M 98% ^{15}N-enriched nitric acid in D_2O).

various isomers of **11** are well separated from the other ^{13}C resonances, and four such methyl signals are present (Table III). The central methylene carbon of the trimethylene units can also be easily identified at 25.2 and 25.9 ppm. In **11b, 11c,** and **11d,** the central methylene groups of the six-membered rings have nearly similar environments and are remote from the sites of the molecules which are central to the isomerism. Thus, they give rise to one signal.

The five resonances in the region of 50–63 ppm are assigned to the methylene groups attached to a secondary or a quaternary sp^3-hybridized nitrogen atom, and of seven such possible methylene groups for **11,** only five were detected, possibly because of coincidences. The low-field portion of the spectrum shows three resonances at 141.2, 147.7, and 158.3 ppm. The peak at 141.2 ppm is assigned to the sp-hybridized carbon of the carbodiimide group of **11a.** Of the three possible sp^2-hybridized carbon atoms in **11b, 11c,** and **11d,** only two (δ 147.7 and 158.3) were found.

The ^{15}N NMR spectrum of **11** in dimethyl sulfoxide was obtained at room temperature. Nine ^{15}N resonances could be unambiguously located and assigned to the various isomers believed to be present. Four of these signals arise from ^{15}NH groups (see Table III), and because each isomer of **11** has only one NH group, the presence of the four ^{15}NH signals accords with the presence of at least four structural isomers of **11** in dimethyl sulfoxide. Except for **11a,** the other isomers possess guanidine-type C=N groups and the ^{15}N chemical shifts of these nitrogens are expected to appear at lower field (<200 ppm). The two ^{15}N signals at 164.6 and 183.5 ppm can be assigned to two such C=N groups, but the third resonance could not be located either because of coincidences or because it corresponds to an isomer in such a low concentration as to give a poor signal-to-noise ratio.

Unfortunately, **11** is not very soluble in nonpolar solvents and appears to undergo complex structural changes in polar, hydrogen-bonding solvents such as chloroform.

Alkylation of Carbodiimides. Although *N*-methyl-*N,N'*-di-*tert*-butylcarbodiimidium ions **12** and **13** are well-known reagents in organic synthesis,[19,20] there have been

Table IV. Nitrogen-15 Resonances[a] for Cyclic Dimers 15

R	X	registry no.	solvent	N1	N2, 3	N4
cyclohexyl	I	66922-50-7	CH_3I	139.7	235.3, 237.6	258.2
	CH_3SO_4	66922-52-9	$(CH_3)_2SO_4$	138.9	235.0, 236.8	257.9
isopropyl	CH_3SO_4	39734-83-3	$(CH_3)_2SO_4$	135.8	234.9, 236.6	257.2

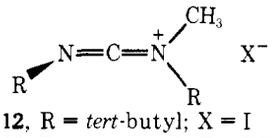
[a] In parts per million *upfield* from external nitric acid (1 M 98% ^{15}N-enriched nitric acid in D_2O).

Table V. Carbon-13 Resonances[a] of Cyclic Dimers 15

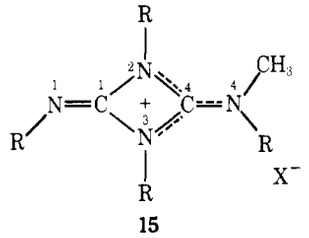
R	X	$^{13}C_4{=}N_4$	$^{13}C_1{=}N_1$	other ^{13}C's
isopropyl	CH_3SO_4	164.3	135.1	19.5, 20.5, 20.7, 23.9 (CH_3's of isopropyl); 31.0 (CH_3SO_4); 50.0 (CHN_1); 50.8 (CH's of N2 and N3); 53.7 (CH_3N_4); 54.2 (CHN_4)
cyclohexyl	CH_3SO_4	164.6	134.6	Not assigned

[a] In parts per million downfield from internal tetramethylsilane.

disagreements over the structure of other *N,N,N'*-trialkylcarbodiimidium ions. Scheffold and Saladin[21] reported that *N*-methyl-*N,N'*-dicyclohexylcarbodiimidium iodide (**14**) can be prepared by prolonged heating of *N,N'*-dicyclohexylcarbodiimide (**3**) in methyl iodide. Hartke and co-workers[19,22] demonstrated that only *N,N'*-di-*tert*-butylcarbodiimide can be converted to the corresponding trialkylcarbodiimidium ions. Other less-hindered *N,N'*-dialkylcarbodiimides, including **3**, have been reported[19,22] to react with alkylating agents such as methyl iodide and dimethyl sulfate to form virtually exclusively cyclic dimer **15**.



12, R = *tert*-butyl; X = I
13, R = *tert*-butyl; X = BF_4
14, R = cyclohexyl; X = I



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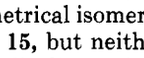
We have used ^{15}N and ^{13}C NMR to follow the alkylation of diisopropylcarbodiimide (**2**) and dicyclohexylcarbodiimide (**3**). The ^{15}N spectrum of **3** in methyl iodide at room temperature shows only one resonance at 275.0 ppm (Table I). When a mixture of **3** and methyl iodide is refluxed for 50 h,[21] the ^{15}N NMR spectrum (Table IV) shows four new resonances, and nothing corresponding to the original carbodiimide could be detected. It is clear from this that the "quaternization" product is a dimer of structure **15** and not a simple *N,N,N'*-trialkylcarbodiimidium ion. A similar spectrum (Table IV) was obtained by warming a mixture of **3** and dimethyl sulfate at 70 °C for a few minutes. Furthermore, diisopropylcarbodiimide gives rise to a four-line spectrum after reaction with dimethyl sulfate (Table IV) or with methyl iodide. The ^{13}C NMR spectra of **2** and **3**, after treatment with dimethyl sulfate, also show resonances (Table V) consistent with the corresponding cyclic dimers.

The observed nonequivalence of the two (presumably planar) guanidino nitrogens, N2 and N3, in cyclic dimers **15** (Tables IV and V) could be the result of geometrical isomerization[18] about the $C_1{=}N_1$ double bond or slow rotation about the



partial double bond. If both of these processes are slow at room temperature, two geometrical isomers, namely syn and anti, would be expected for **15**, but neither the ^{13}C nor the ^{15}N NMR spectra of the cyclic dimers (**15**) suggest the presence of more than one isomer. Thus, one of the interconversion processes has to be fast on the NMR time scale at room temperature, or else both processes are slow at room temperature, and either the syn or the anti isomer is highly favored.

Registry No.—**9**, 66922-55-2; **11a**, 25952-53-8; **11b**, 66932-92-1; **11c**, 66922-56-3; **11d**, 66922-57-4.

Supplementary Material Available. Natural-abundance level ^{13}C and ^{15}N NMR spectra of compound **11** in dimethyl sulfoxide and the ^{15}N spectrum of the cyclic dimers (**15**) (2 pages). Ordering information is given on any current masthead page.

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Natural-Abundance Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Electronic Effects in Benzenesulfonamides[1a]

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The ^{15}N chemical shifts of a number of benzenesulfonamides with different substituents at nitrogen have been measured in dimethyl sulfoxide solution and compared to those of similarly substituted benzenamines and ethanamides. The relative extent of phenyl–sulfur and nitrogen–sulfur p_π–d_π orbital overlap is discussed. Substitution of $C_6H_5SO_2$ for one benzyl group of *N,N*-dibenzylethanamide results in considerable lowering of the free energy of activation of the N–CO bond rotation.

Physical studies of sulfonamides have included analyses of the sulfur–oxygen and sulfur–nitrogen vibrational modes in the infrared spectrum[2-4] and of X-ray[5] and dipole moment[6] data of selected species. The pK_a values of a few secondary arylsulfonamides also have been reported, and the effect of N-substituents on acidity has been discussed.[7] A quantitative estimate of the electronic effect of the sulfamoyl group itself has been derived from the ^{19}F chemical shifts of fluorobenzenesulfonamides[8] and from the acidity constants[9] of appropriately substituted benzoic acids and benzeneammonium ions.

This paper presents the results of an ^{15}N NMR study of arylsulfonamides.

Results and Discussion

The ^{15}N chemical shifts of a series of sulfonamides, measured as 9.0 mol % solutions in dimethyl sulfoxide at the natural-abundance level, are summarized in Table I together with one-bond N–H coupling constants.

Constraint of alkyl groups at nitrogen in *N,N*-dialkylbenzenesulfonamides through the formation of a five-membered ring (**8** to **9**) has no appreciable effect on the position of the ^{15}N resonance, while ring expansion (**9** to **11**) causes only a small downfield shift (−1.1 ppm). The downfield shifts observed with increased alkyl substitution at nitrogen in benzenesulfonamides (**2** to **4** to **13**) are comparable to those observed for similar structural changes in ethanamides in the same solvent,[10] as is the shift resulting from replacement of one hydrogen by an electron-withdrawing phenyl group (**2** to **18**, −26.2 and −29.9 ppm for the benzensulfonamide and ethanamide systems, respectively). The effect of branching at an alkyl carbon atom α to nitrogen in the sulfonamides (**3** to **5**, −9.0 ppm) is identical in magnitude and direction with that in ethanamides ($CH_3CONHC_2H_5$ to $CH_3CONHCH(CH_3)$-C_2H_5, −8.9 ppm) despite the fact that the downfield shift resulting from β substitution (**8** to **10**) is only about one-tenth of that found for ethanamides and alkanamines. On the whole, the data demonstrate the similarity of substituent and steric effects at nitrogen in the *N*-alkylsulfonamides and ethanamides.

4-Substituted *N*-phenylbenzenesulfonamides with increasingly strong electron-withdrawing groups at the 4 position of the *N*-aryl moiety exhibit progressively lower field shifts of the ^{15}N resonance. These shifts only partially follow the trends in the corresponding pK_a values (Table II).

Exchange of the NH hydrogens was observed for the more acidic *N*-phenylbenzenesulfonamides. Thus, the doublets in the proton-coupled ^{15}N spectra of **18–22** changed to a broad singlet with 4-CN (**23**) and to a sharp singlet with 4-NO_2 (**24**) as the result of proton exchange becoming fast on the NMR time scale.

The one-bond NH coupling constants appear to follow no definable trends except that their absolute magnitudes are consistently higher for secondary than for primary sulfonamides.

^{15}N Shift Correlations with Substituent Parameters. The extent of nitrogen lone-pair delocalization into the 4-X-substituted phenyl ring in the general system, Q–NH–C_6H_5-4-X, can be evaluated reasonably well from a linear correlation of ^{15}N shifts with the Taft dual substituent parameters[8] according to eq 1,

$$\delta(^{15}N)_{X=X} = \rho_I\sigma_I + \rho_R\sigma_R^- + \delta(^{15}N)_{X=H} \quad (1)$$

where σ_I and σ_R^- are the inductive and resonance (benzenamine-type) parameters, respectively, for the substituent, X, while the coefficients ρ_I and ρ_R reflect the sensitivity of the ^{15}N shifts to these substituent effects. Because the nitrogens of *N*-phenylbenzenesulfonamides are expected to be electronically similar to those of benzenamines and *N*-phenylamides, it seemed likely that correlations based on σ_I and σ_R^- might be possible for each of these kinds of systems.

The substituted benzenamine shifts, taken from Axenrod's study[11] (^{15}N shifts relative to internal benzenamine, 1 M in dimethyl sulfoxide) and referenced to external HNO_3, are listed in Table III. The ^{15}N shifts of *N*-phenylethanamides are also taken from the literature.[10] The constants ρ_I and ρ_R are given in Table IV together with the correlation coefficient *r*, the root mean square error (rms), and the number of data points (*n*) for each correlation.

It is apparent that the sensitivity of the ^{15}N shifts to electronic substituent effects in N–C_6H_4–4-X decreases markedly in the series: benzenamines > *N*-phenylbenzenesulfonamides > *N*-phenylethanamides. That this may be due to increased delocalization of the electron pair on nitrogen into Q of Q–

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