methyl-4-(4-*tert*-butylphenyl)-1-butyne (0.08 g, 6%) eluted last. Spectral data for 4 (*p*-*t*-Bu) are given in Table II.

Preparation of 4 (X = 3,5-$(CH_3)_2$). A solution of LiTMP prepared from 8.2 mL of 1.6 M methyllithium and 1.90 g of tetramethylpiperidine was added dropwise to a solution of 1.30 g of 3,5-dimethylbenzyl bromide in 6 mL of 1,1-dimethylallene and 3 mL of ether. After 30 min, a standard aqueous workup followed. After the organic phase was dried over Na_2SO_4, the solvent was removed by a rotary evaporator. The residue was chromatographed on 20 g of silica gel with Skelly F elution. A mixture of 4 and 5 (X = 3,5-$(CH_3)_2$) eluted first and weighed 0.47 g (37%). The ratio of 4 to 5 was about 3:1 by NMR. An acetylene product, 3,3-dimethyl-4-(3,5-dimethylphenyl)-1-butyne (0.18 g, 14%), eluted last. Spectral data for 4 (3,5-$(CH_3)_2$) are given in Table II.

Preparation of 4 (X = *m*-$SiMe_3$). A solution of LiTMP prepared from 9.6 mL of 1.4 M methyllithium and 1.90 g of tetramethylpiperidine was added dropwise to a solution of 1.60 g of *m*-(trimethylsilyl)benzyl bromide in 6 mL of 1,1-dimethylallene. After 30 min, a standard aqueous workup followed. After the mixture was dried over Na_2SO_4, the solvents were removed by a rotary evaporator. The entire residue was chromatographed on 18 g of silica gel. A mixture of 4 and 5 (X = *m*-$SiMe_3$) eluted first and weighed 0.61 g (40%). The ratio of 4 to 5 was approximately 4:1 as determined by NMR. An acetylene product, 3,3-dimethyl-4-[3-(trimethylsilyl)phenyl]-1-butyne (0.07 g, 5%), elutes last. Spectral data for 4 (*m*-$SiMe_3$) are given in Table II.

Thermal Rearrangement of 4. Kinetics Procedure. Approximately 100 mg of 4 was dissolved in isooctane and sealed in an NMR tube under nitrogen. The tube was heated in a constant-temperature bath for a given amount of time and periodically analyzed for remaining 4 by integration of the olefinic signal at δ 5.5–5.7. Rate constants were calculated by the method of least squares. Correlation coefficients were in all cases greater than 0.999 and in most cases greater than 0.9999. For product analyses, samples of 5 were isolated by preparative gas chromatography or by distillation of the thermolysis products after 10 half-lives.

In the cases of some of the more volatile methylenecyclopropanes (*p*-H, *p*-F, *m*-CF_3, *p*-CF_3), kinetics were monitored by gas chromatography by analysis for unreacted 4 vs. an internal standard (biphenyl). A 20-mg sample was dissolved in 2 mL of isooctane with 35 mg of biphenyl, and portions were sealed in tubes under nitrogen. The tubes were immersed in a constant-temperature bath, and at appropriate time intervals, the contents of the various tubes were analyzed by gas chromatography on a 5-ft, 5% SE 30 column. Rate constants were calculated by standard procedures.

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Registry No. 4 (X = *p*-CN), 72138-30-8; 4 (X = *p*-SCH_3), 72138-31-9; 4 (X = *p*-CO_2CH_3), 72138-32-0; 4 (X = *p*-OCH_3), 65108-27-2; 4 (X = *p*-$Si(CH_3)_3$), 72138-33-1; 4 (X = *p*-Br), 65354-66-7; 4 (X = *p*-*t*-Bu), 72138-34-2; 4 (X = *p*-Cl), 65354-61-2; 4 (X = *p*-CH_3), 65108-26-1; 4 (X = *p*-CF_3), 72138-35-3; 4 (X = 3,5-$(CH_3)_2$), 72138-36-4; 4 (X = *m*-$SiMe_3$), 72138-37-5; 4 (X = *m*-CH_3), 72138-38-6; 4 (X = H), 65108-25-0; 4 (X = *m*-OCH_3), 65354-64-5; 4 (X = *m*-Cl), 65354-63-4; 4 (X = *m*-F), 65354-65-6; 4 (X = *m*-CF_3), 72138-39-7; 4 (X = *p*-F), 72138-40-0; 4 (X = 3,5-Cl_2), 72138-41-1; 4 (X = *m*-CN), 72138-42-2; 5 (X = *p*-SCH_3), 72138-43-3; 5 (X = *p*-$SiMe_3$), 72138-44-4; 5 (X = *p*-*t*-Bu), 72138-45-5; 5 (X = 3,5-$(CH_3)_2$), 72138-46-6; 5 (X = *m*-$SiMe_3$), 72138-47-7; *p*-(thiomethoxy)benzyl chloride, 874-87-3; 1,1-dimethylallene, 598-25-4; *p*-(trimethylsilyl)benzyl bromide, 17903-42-3; 3,3-dimethyl-4-[4-(trimethylsilyl)phenyl]-1-butyne, 72152-04-6; *p*-*tert*-butylbenzyl chloride, 19692-45-6; 3,3-dimethyl-4-(4-*tert*-butylphenyl)-1-butyne, 72138-48-8; 3,5-dimethylbenzyl bromide, 27129-86-8; 3,3-dimethyl-4-(3,5-dimethylphenyl)-1-butyne, 72138-49-9; *m*-(trimethylsilyl)benzyl bromide, 17903-42-3; 3,3-dimethyl-4-[3-(trimethylsilyl)phenyl]-1-butyne, 72138-50-2.

Proximity Effects on Nitrogen-15 Chemical Shifts of 8-Substituted 1-Nitronaphthalenes and 1-Naphthylamines[1a]

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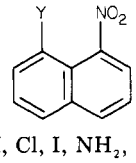
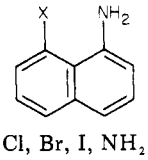
^{15}N chemical shifts of several 8-substituted 1-nitronaphthalenes and 8-substituted 1-naphthylamines have been determined and, in general, the substituent effects are unexpectedly small. The high-field shift of the amine nitrogen of 8-nitro-1-aminonaphthalene may indicate a degree of σ complexing between the amino group and the proximate substituents of the type suggested by Dunitz. The smallness of the other substituent effects may be the result of mutual cancellation of opposing larger effects.

Although the steric interactions of proximate alkyl groups are generally well understood and, in fact, often are reliably predictable by molecular mechanics calculations, the interactions of proximate polar groups are less well understood because of the possibility of complex electrical interactions in addition to simple steric effects.

We report here the ^{15}N chemical shifts of 1,8-disubstituted naphthalenes 1 and 2 where it is well established that large proximate effects are to be expected.[2] In the absence of proximity effects, the ^{15}N shifts of these compounds are



1, Y = H, Cl, I, NH_2, NO_2, CN



2, X = H, Cl, Br, I, NH_2, NO_2, CN

reasonably expected to correlate with the electronic properties of the substituents X and Y which occupy "meta-like" positions. Large deviations of the ^{15}N shifts from those expected can be assumed to be the result of

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(2) For a review, see V. Balasubramaniyan, *Chem. Rev.*, 66, 567–641 (1966).

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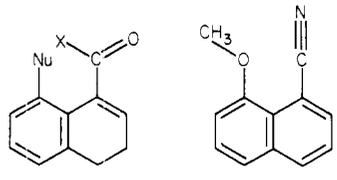
nonbonded repulsions, dipole–dipole interactions, charge-transfer processes, hydrogen bonding, or perhaps even covalent bonding. Obviously, these effects will depend strongly on the nature and spatial disposition of the substituents. Unfortunately, relatively few geometries of peri-substituted naphthalenes have been reported.[2] However, from the available data it is clear that steric repulsion between the 1- and 8-substituents can lead to considerable deformations of the normal valency angles, as with 1,8-dinitronaphthalene (1, Y = NO_2), in which the C–N bonds are splayed to increase an otherwise short, nonbonded N···N distance. In this compound, the nitro groups are rotated about the C–N axis by 45° and are displaced from the aromatic plane in opposite directions, as are carbons 1 and 8. Values of the torsional angle of the nitro group in the series of compounds 1 have been calculated by Dashevskii[3] from appropriate potential energy functions to be 47° (Y = H), 54° (Y = NO_2), 37.9° (Y = Cl), 43.1° (Y = Br), and 30° (Y = F). These torsional angles were calculated to be associated with 18–20° and 6–7° out-of-plane displacements of the C–Y and C–N bonds, respectively.

Geometries for the series of compounds 2 have not yet been reported, but a potential energy calculation[4] for 1-naphthylamine itself (2, Y = H) predicts coplanarity of the amino group and aromatic rings. However, analysis of ultraviolet absorptions of the substance suggests a twisted amino group, and, furthermore, a torsional angle of 28° has been reported[5] for this compound from the molar Kerr constants.

Of great interest to us here is recent evidence for donor–acceptor interactions in 1,8-disubstituted naphthalenes obtained by Dunitz[6] from crystallographic analysis. Unidirectional, 5°, in-plane distortions of the exocyclic bonds carrying the nucleophilic (Nu) and electrophilic substituents have been determined for 3 and 4, and these have



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4

been attributed to electrophile–nucleophile interactions between the substituents, which are postulated to provide useful models of the transition states for nucleophilic addition to carbonyl or nitrile multiple bonds.

It was the purpose of the present work to determine whether ^{15}N NMR spectroscopy could provide insight into the nature of the proximity effects of substances such as 1 and 2, because it is well established that nitrogen chemical shifts can be very sensitive to changes in molecular structure.

Results and Discussion

Table I summarizes the ^{15}N chemical shifts (relative to internal nitrobenzene) of the 8-substituted 1-nitronaphthalenes, 1, and, for comparison, 3-substituted nitrobenzenes. Table II gives ^{15}N shifts (relative to external nitric acid) of the 8-substituted naphthylamines, 2, and again for comparison, 3-substituted anilines[7] as well as the

Table I. ^{15}N Chemical Shifts of 8-Substituted 1-Nitronaphthalenes, 1, and 3-Substituted Nitrobenzenes in Chloroform

	$\delta\ ^{15}N^a$	
Y	1	3-$YC_6H_4NO_2$
NO_2	−2.0	6.0
CN	−1.7 (−1.9)[b]	5.5
Br	[c]	3.4
I	−4.2	3.3
Cl	−7.7	3.3
H	−4.0	0.0
NH_2	−12.7	−1.2

[a] In ppm from nitrobenzene. Positive values are shifts upfield from nitrobenzene. [b] Assignments uncertain. A mixture of the 1,8 and 1,5 isomers was used. [c] Insoluble in chloroform.

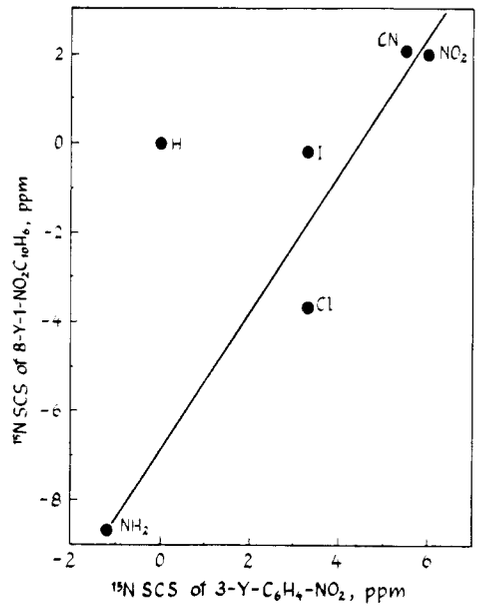

Figure 1. Correlation of substituent ^{15}N chemical shifts of 8-Y-1-nitronaphthalenes with 3-Y-1-nitrobenzenes (substituent chemical shifts, SCS, are in ppm relative to Y = H).

proton shifts of the amino group in 2 and one-bond NH coupling constants.

The overall effects of the substituents Y and X on the ^{15}N shifts of 1 and 2 are quite surprisingly small, at most 13 ppm, despite the very close proximity of the groups being studied. Comparable, if not larger, influences are associated with the ^{15}N shifts of a piperidine nitrogen to which an equatorial or axial alkyl group is attached.[8] The smallness of the shift changes suggests that opposing influences are involved. The ^{15}N chemical shifts of the nitro group in the nitronaphthalenes, 1, are roughly parallel to those of the corresponding meta-substituted nitrobenzenes (see Table I and Figure 1) which correlate with σ_m. The exception is the shift of unsubstituted 1-nitronaphthalene which is perhaps 6 ppm more upfield than expected from the shifts of the other compounds. This result may be due to a smaller steric effect of hydrogen relative to that of all other substituents, Y, at C8, which allows the nitro group to be nearly coplanar[9] with the aromatic ring and results in more extensive aryl–nitro group conjugation. Alternatively, the ^{15}N shifts of all of the other compounds of type

(3) V. Dashevskii, Yu. T. Struchkov, and Z. A. Akopyan, *Zh. Strukt. Khim.*, 7, 555–61 (1966).
(4) K. Skigawa, *Zh. Strukt. Khim.*, 12, 703–7 (1971).
(5) R. J. W. LeFevre and A. Sundaram, *J. Chem. Soc.*, 4756–70 (1962).
(6) J. D. Dunitz, private communication, July 20, 1978.
(7) T. Axenrod, P. S. Pregosin, M. J. Wieder, E. D. Becker, R. B. Bradley, and G. W. A. Milne, *J. Am. Chem. Soc.*, 93, 6536–41 (1971).
(8) R. O. Duthaler, K. L. Williamson, D. D. Giannini, W. H. Bearden, and J. D. Roberts, *J. Am. Chem. Soc.*, 99, 8406–12 (1977).
(9) A torsional angle of 49° has been reported for the nitro group in crystalline 1,5-dinitronaphthalene which has the same 1,8-substituents as 1-nitronaphthalene. It appears that if the nitro group is to be coplanar with the ring in solution, some molecular deformations will be necessary.

Table II. ^{15}N and ^{1}H Chemical Shifts and One-Bond NH Coupling Constants of the NH_2 Group in 8-X-Substituted 1-Naphthylamines and of 3-X-Substituted Anilines

	^{15}N $(NH_2)^a$ data			$^{1}H^b$ data					
	2			NH_2					
				3-$XC_6H_4NH_2$ ^{c}		2			H2 of 2
X	$CHCl_3$	Me_2SO	3-$XC_6H_4NH_2$ ^{c} Me_2SO	Me_2SO	$^{1}J_{^{15}NH}$ ^{d}	$CHCl_3$	Me_2SO	$^{1}J_{^{15}NH}$ ^{e}	Me_2SO
NO_2	318.3	313.9	310.2	5.75	86.2	4.04	4.92	79.9 (87.0)	7.16
CN		313.3 ^{f}	311.5 ^{f}	5.51	86.6 ^{h}	4.88	6.13	82.5 ^{i} (87.4)	6.85
Cl	314.2	308.6	312.6	5.30	85.1	5.10	5.98	j (85.9)	6.77
Br	313.3	308.3	312.8	5.30	85.3	5.11	6.00	86.0 (86.1)	6.83
I	311.8	307.2	313.4	5.20	84.4	4.90	5.83	82.5 (85.2)	6.83
H	323.0	315.7	315.1	4.90	82.6	4.02	5.63	83.4 (83.4)	6.70
NH_2	314.6	310.6	315.9 ^{g}	4.55 ^{g}	81.5 ^{h}	4.46	5.38	79.5 (82.3)	6.53

^{a} In ppm upfield from external 1 M $D^{15}NO_3$ in D_2O. ^{b} Chemical shifts are in ppm downfield from tetramethylsilane. ^{c} Reference 7. ^{d} Coupling constants, in Hz, of 3-X-substituted anilines.[7] ^{e} In Hz. The values in parentheses are those predicted from electronic effects on J(NH) of the corresponding anilines. ^{f} The shift of the 1,5 isomer was 312.5 ppm. ^{g} This work. ^{h} Estimated from the correlation of $^{1}J_{^{15}NH}$ with σ.[7] ^{i} Kindly measured for us by Dr. C. Dyllick-Brenzinger. ^{j} A single signal was observed because of fast proton exchange with the medium.

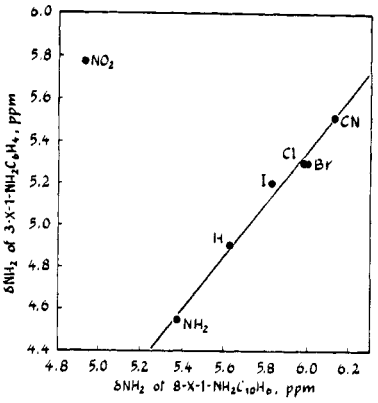

Figure 2. Correlation of NH_2 ^{1}H shifts of 3-X-anilines and 8-X-1-naphthylamines in dimethyl sulfoxide solution.

1 may move more than 6 ppm *downfield* as the result of steric interactions in which the angle between the direction of the interaction and the bond to the nitrogen of the nitro group is less than 90°.[10]

The ^{15}N shifts of the amino group in the 8-substituted 1-naphthylamines **2**, where X is other than H, are *downfield* of that of 1-naphthylamine. This suggests again the possibility of a pervasive downfield steric effect arising from 8-substituents other than hydrogen.[11] Furthermore, although the ^{15}N shifts of aniline and 3-halogen-substituted anilines correlate with substituent electronic effects, the trend of the ^{15}N shifts of the corresponding 1-naphthylamines **2** appears to be mainly a function of substituent size (see Table II).[12] This trend is not in a direction expected for inhibition of NH_2-aryl resonance by large 8-substituents, and, moreover, the shifts of H2 of series **2**, which might be expected to be sensitive to variations in the torsional angle of the amino group, correlate better with the usual electronic effects of the substituents X (with which the ortho hydrogen is formally conjugated) than with effective size. The variation in the ^{15}N shifts, therefore, seems best attributed to straightforward steric effects.

Despite the large steric and electron-withdrawing effects predicted for the nitro group, the $^{15}NH_2$ shift of 8-nitro-1-naphthylamine is only 3.3 ppm upfield from that of 1,8-diaminonaphthalene. This shielding is in the same direction as the hydrogen-bonding (+1.5 ppm) and protonation (+5.6 ppm) shifts found for aniline[13] and can reasonably be expected to correspond to σ complexing between the amino group and the electrophilic substituent. The exceptionally low value of the one-bond NH coupling constant of 8-nitro-1-naphthylamine—79.9 Hz relative to the 87.0 Hz predicted from substituent effects (Table II)—is in the direction expected for sp^3 hybridization[14] of the amino nitrogen and is therefore also strongly suggestive of donor–acceptor bonding.

The influences on the ^{15}N chemical shifts of the 8-substituted 1-naphthylamines do not seem to be reflected in the proton shifts of the amino groups in **2**. This is not surprising in view of the different shielding mechanisms which are invoked to explain the shifts of proton and ni-

(10) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, 86, 2984–90, (1964).

(11) The shift for 1-naphthylamine itself seems to be at least 5 ppm upfield of what might be expected from the shifts of the other compounds in the series (see Figure 1).

(12) The sequence of shifts for Cl, Br, and I as substituents are opposite for the two series.

(13) R. O. Duthaler and J. D. Roberts, *J. Am. Chem. Soc.*, 100, 3889–95 (1978).

(14) See "Nitrogen NMR", M. Witanowski and G. A. Webb, Eds., Plenum Press, New York, 1973, pp 269–70, for references and discussion.

trogen nuclei.[15] There is, however, a good correlation (Figure 2) between the amino proton shifts of the naphthylamines and corresponding anilines. The exception is again the shift of 8-nitro-1-naphthylamine, which is too far upfield by about 1.4 ppm. This shielding is too large to be the result of the magnetic anisotropy of an out-of-plane nitro group alone and is in the proper direction for sp^3 hybridization of the amino group nitrogen resulting from $NH_2 \cdots NO_2$ σ complexing.

Experimental Section

Materials. The nitronaphthalenes 1 (Y = H, Cl, NO_2) were commercial materials and were used without further purification. Commercial 1-naphthylamine was recrystallized from dilute ethanol and dried in vacuo. 1,8-Diaminonaphthalene was partially purified by chromatography, eluting through neutral alumina with chloroform. It was then recrystallized from dilute ethanol and dried in vacuo. 8-Nitro-1-naphthylamine (1, Y = NH_2) was synthesized from 1-naphthylamine by a published procedure[16] and purified by recrystallization from ligroin. 8-Iodo-1-nitronaphthalene (1, Y = I) was prepared from 8-nitro-1-naphthylamine by diazotization and treatment with potassium iodide.[17] 8-Nitro-1-naphthonitrile (1, Y = CN) was synthesized by nitration[16] of 1-naphthaldehyde below 10 °C with a mixture of 70 and 90% nitric acid. The yellow product, which was a 50:50 mixture of the 8- and most likely the 5-nitro-1-naphthaldehydes, was recrystallized from ethyl acetate and then converted to the oximes, which were subsequently dehydrated[18] to give a mixture of 8- and 5-nitro-1-naphthonitriles. The NMR spectra were taken of the mixture of nitriles. 8-Bromo-1-nitronaphthalene (1, Y = Br) was prepared from 8-bromo-1-naphthylamine by diazotization and subsequent treatment with copper and sodium nitrite. The product was isolated by extraction with boiling methanol. No ^{15}N NMR spectrum of this compound could be obtained in chloroform because of its low solubility.

The 8-substituted naphthylamines (2, X = Cl, I, CN) were prepared from the corresponding nitronaphthalenes by reduction with sodium hydrosulfite according to the method of Hodgson.[17] The products were purified by recrystallization from ligroin. A 50:50 mixture of 8- and 5-nitro-1-naphthonitriles was reduced to give a 2:1 mixture of amines after several recrystallizations from ligroin. The percent composition was determined by integration of the separate amine proton signals of the isomers in the mixture. 8-Bromo-1-naphthylamine (2, X = Br) was synthesized from 1,8-diaminonaphthalene by published procedures.[20,21]

Chloroform, used as solvent in the determination of NMR spectra, was dried over anhydrous potassium carbonate, distilled, and then stored over molecular sieves. Dimethyl sulfoxide was dried for several days over calcium hydride and then distilled prior to use.

NMR Spectra. The ^{15}N NMR spectra were obtained by using a Bruker WH-180 NMR spectrometer operating at 18.25 MHz as previously described.[22] Spectra of 6–9 mol % solutions of the naphthylamines in chloroform or dimethyl sulfoxide were obtained by using a pulse width of 15 μs with continuous proton noise decoupling, a repetition rate of 1.2 or 3 s, 8K data points, and an average of 4000 accumulations at a sweep width of 7000 Hz. The shifts were measured relative to external 1 M $D^{15}NO_3$ in D_2O, and the temperature was held near 25 °C. The shifts were corrected to this temperature in cases where the probe temperature deviated from this value. The shifts can be converted to the ammonia scale[23,24] by the relation $\delta\ ^{15}N(^{15}NH_3) = 375.80$ ppm $- \delta\ ^{15}N(H^{15}NO_3)$.

The ^{15}N spectra of the nitronaphthalenes were recorded of 6 mol % solutions in chloroform containing 0.47 mol % of chromium tris(acetylacetonate) to reduce the long relaxation times of the nitro group nitrogens. Shifts were measured relative to internal nitrobenzene (9 mol %) at temperatures of 30–40 °C to keep the naphthalenes in solution and were then corrected to a temperature of 25 °C. A 5-mm tube containing a 1 M solution of tetramethylammonium-^{15}N chloride in D_2O and held within the sample tube by a Teflon support provided the field-frequency lock as well as an additional external reference. Useful spectra were obtained with a pulse width of 32 μs and a pulse delay of 0.8 s with 5000 accumulations, 8K data points, and a sweep width of 10 000 Hz. Increasing the concentration of the relaxation agent had no effect on the shifts of the nitronaphthalenes relative to internal nitrobenzene but caused them to be moved downfield relative to the external upfield reference.

Proton spectra of the naphthylamines in deuteriochloroform and in dimethyl-d_6 sulfoxide were taken with a Varian EM-390 NMR spectrometer operating at 90 MHz.

Registry No. 1, Y = NO_2, 602-38-0; 1, Y = CN (1,8 isomer), 2024-82-0; 1, Y = CN (1,5 isomer), 23245-64-9; 1, Y = I, 14447-51-9; 1, Y = Cl, 602-37-9; 1, Y = H, 86-57-7; 1, Y = NH_2, 3229-89-8; 2, X = CN (1,8 isomer), 38515-13-8; 2, X = CN (1,5 isomer), 72016-73-0; 2, X = Cl, 59107-51-6; 2, X = Br, 62456-34-2; 2, X = I, 52753-62-5; 2, X = H, 134-32-7; 2, X = NH_2, 479-27-6; 3-NO_2-$C_6H_4NO_2$, 99-65-0; 3-CN-$C_6H_4NO_2$, 619-24-9; 3-Br-$C_6H_4NO_2$, 585-79-5; 3-I-$C_6H_4NO_2$, 645-00-1; 3-Cl-$C_6H_4NO_2$, 121-73-3; $C_6H_5NO_2$, 98-95-3; 3-NH_2-$C_6H_4NO_2$, 99-09-2; 3-NH_2-$C_6H_4NH_2$, 108-45-2.

(15) However, see ref 7.
(16) H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1844–8 (1936).
(17) H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, 327–31 (1947).
(18) "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, p 622.
(19) A. I. Vogel, "A Textbook of Practical Organic Chemistry", 3rd ed., Longmans, London, p 612.
(20) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **61**, 136–42 (1939).
(21) L. H. Klemm, J. W. Sprague, and E. Y. K. Mak, *J. Org. Chem.*, **22**, 161–6 (1957).
(22) D. Gust, R. B. Moon, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 4696–5700 (1975).
(23) J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 735–7 (1974).
(24) G. C. Levy and R. L. Lichter, "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", Wiley-Interscience, New York, 1979, pp 28–31.