TABLE I: Comparison of Characteristic Data of Photochromic Systems Measured in Solution

characteristic	spiropyranes[19]	HOCD/ HOCDPO/DCA
$\Delta\lambda$ colored/colorless, nm	200-300	260
Q(colorization)	0.01-1, typ[a] 0.1-0.5	0.4
Q(decolorization)	0-0.2, typ 0.01-0.05	0.08
reversibility	5-17000, typ 100-1000	3000
thermal stability (20 °C)	5 s-5 days	170 yr
faceless/photoreversible photochromic	either or	both on choice

[a] typ denotes typically.

in both photochemical color reactions light is converted effectively.

The photochromic effect described in this paper is not limited only to fluid solutions. It can also be observed in rigid matrices, for example, in poly(vinyl chloride). Up to now, however, quantitative experiments were not carried out in such environments.

Finally, the novel photochromic system reported in this paper is compared with respect to the most important properties for an application with the spiropyranes, which are the most advanced class of photochromic compounds known to date. This is done in Table I.

With respect to the wavelength shift $\Delta\lambda$, the quantum yields of colorization and decolorization, and the reversibility, the novel photochromic system is just as good as the spiropyranes.

However, a decisive advantage is its better stability by a factor of 10^4 for the thermally labile component. Exposed photochromic films based on spiropyranes have to be stored in refrigerators, in order to prevent a loss of information via thermal bleaching. This provision would not be necessary for photochromic films of the novel system.

A further important preference of our photochromic system is the possibility of the choice between photoreversibility (irradiation of the sensitizer or the endoperoxide) and photoresistancy (irradiation of the colored compound). In this way reading without simultaneous slow loss of the information is accomplished. To our knowledge the photochromic system presented here is the first photoreversible one to offer this possibility.

Further systematic studies on endoperoxides will point out whether further improvements in the photochromic properties of this class of compounds can be reached.

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Nitrogen-15/Nitrogen-14 Isotope Effects on the Carbon-13 Nuclear Magnetic Resonance Chemical Shifts of Azobenzene and Benzo[*c*]cinnoline

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The previously found $^{15}N/^{14}N$ isotope effects on the ^{13}C chemical shifts of the ipso positions (C1) of azobenzene-^{15}N and benzo[*c*]cinnoline-^{15}N in neutral and strong acid solutions were reinvestigated more precisely by observing the $^{15}N/^{14}N$ isotope shifts of the mixtures of $^{14}N_2$, $^{15}N_1$, and $^{15}N_2$ compounds. Abnormal results of the isotope effects in *cis*-azobenzene-^{15}N and benzo[*c*]cinnoline-^{15}N—that is, the ipso carbon bonded to ^{15}N, C1(^{15}N), resonates at a lower field than that bonded to ^{14}N, C1(^{14}N)—were found to be due to reversal of the assignments between the two ipso carbons. Although interchange of the assignments resulted in a normal direction of the isotope shifts, this procedure alternatively led to an anomalously large ^{13}C–^{15}N one-bond coupling constant for a nitrogen atom having an s-hybridized lone pair. The reason that the chemical shift separation between C1(^{14}N) and C1(^{15}N) of the $^{15}N_1$ compound becomes much larger in a strong acid solution than in a neutral solution was found to be explained not by an intrinsic isotope effect but by an isotopic perturbation of a degenerate protonation equilibrium. The equilibrium constant of protonation on the azo nitrogens in the $^{15}N_1$ compound indicated that protonation occurs approximately 5% more preferably on the ^{15}N atom than on the ^{14}N atom; in other words, pK_a of ^{15}N is larger than that of ^{14}N by 0.02 pK_a unit.

Introduction

Isotope effects on chemical shifts in nuclear magnetic resonance spectroscopy are well-known phenomena[2] and have been investigated from both theoretical[3] and experimental[2,4,5] points of view. The former investigations, however, are still limited for small molecules because of difficulty in obtaining knowledge of the dynamic state of

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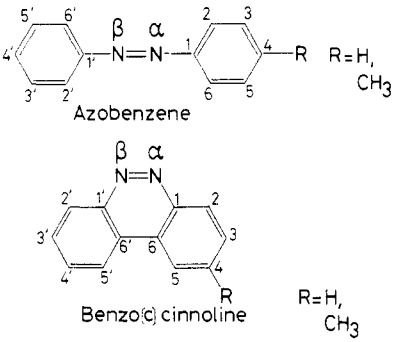

Figure 1. Structures and numbering scheme.

the molecule which can only be obtained from the analysis of vibrational anharmonicity. Thus, much work has been done to obtain the isotope shifts experimentally. However, only a few data concerning the $^{15}N/^{14}N$ isotope effects on ^{13}C chemical shifts are reported.[5]

Previously,[6] in the course of our studies on the $^{13}C-^{15}N$ spin–spin coupling constants of *trans*- and *cis*-azobenzenes and benzo[*c*]cinnoline (Figure 1, R = H), we found the following unexplainable phenomena concerning the $^{15}N/^{14}N$ isotope effects on the ^{13}C chemical shifts in the $^{15}N_1$ compounds: (1) In neutral solutions, the ipso carbon bonded to ^{15}N (designated as C1(^{15}N)) resonates at a higher field than that bonded to ^{14}N (designated as C1(^{14}N)) in the case of *trans*-azobenzene, whereas the situations are reversed in the cases of *cis*-azobenzene and benzo[*c*]-cinnoline. (2) In strong acid solutions, the chemical shift separations between the two ipso carbons increase in magnitude by ca. 6 times as compared to the corresponding separations in neutral solutions.

Usually, C1(^{15}N) is expected to resonate at a higher field than C1(^{14}N), since in most cases substitution by a heavier isotope is known to cause a high-field shift[3,4] and in our cases the $^{15}N/^{14}N$ isotope effect may act far more effectively on the nearer atom from the site of ^{15}N substitution. Accordingly, the observations in *cis*-azobenzene and benzo[*c*]cinnoline are abnormal. Moreover, it seems unlikely that mere protonation on the azo nitrogens exerts so serious effects as to change the dynamic states of these molecules. Therefore, we should consider some special mechanism for explaining observation 2. In an $^{15}N_1$ compound, one of whose two ipso carbons (i.e., C1(^{14}N) and C1(^{15}N)) is more shielded or deshielded than the remaining one, depends, of course, on the assignments of the C1(^{14}N) and C1(^{15}N). Previous assignments were determined by taking into account the rule usually referred to as a one-bond lone-pair effect.[7] This rule states that a $^{13}C-^{15}N$ one-bond coupling constant, ^1J(C–N), is small when it involves a nitrogen atom having an s-hybridized lone pair. To our knowledge there are no exceptions to this rule. Therefore, if we reverse the assignments, we must be content with large ^1J(C–N) values for *cis*-azobenzene (+10.0 Hz)[6] and benzo[*c*]cinnoline (+7.3 Hz).[6]

In the present study, in order to solve these problems, we have observed the chemical shift differences between C1 carbons of the $^{15}N_1$ compounds of *trans*-azobenzene and benzo[*c*]cinnoline and those of the corresponding $^{14}N_2$ and $^{15}N_2$ compounds, since our previous data are the ones obtained within $^{15}N_1$ compounds only.[8] Thus, obtainable

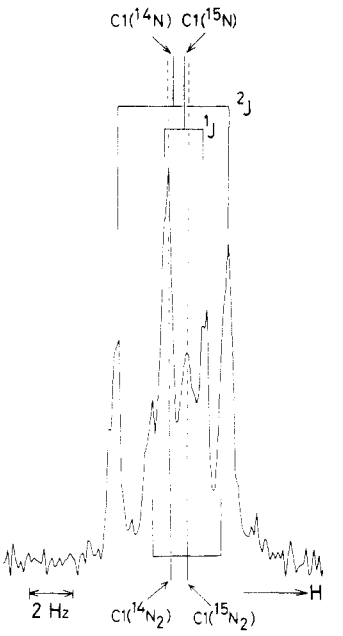

Figure 2. ^{13}C NMR spectrum of ipso (C1) carbons of mixtures of *trans*-azobenzene-$^{14}N_2$ (a), *trans*-azobenzene-^{15}N (b), and *trans*-azobenzene-$^{15}N_2$ (c) in $CDCl_3$, a:b:c = 1:5:2.

relative ordering of the chemical shifts including those of $^{14}N_2$ and $^{15}N_2$ compounds may provide useful information on the assignments. However, to confirm the assignments more directly, we have newly synthesized ^{15}N-monosubstituted 4-methylazobenzene and methylbenzo[*c*]cinnoline (Figure 1, R = CH_3) and observed their $^{13}C-^{15}N$ spin–spin coupling constants in both neutral and strong acid solutions. These isotope shifts including the $^{14}N_2$ and $^{15}N_2$ compounds and the ^nJ(C–N) values of their methyl-substituted compounds would give unambiguous answers to the above two questions.

Experimental Section

Materials. The samples of azobenzene, benzo[*c*]-cinnoline, and their ^{15}N-enriched compounds were taken from the same batches of preparations as those used in the previous work.[6] 4-Methylazobenzene-β-^{15}N[9] was synthesized from aniline-^{15}N (95% enriched, CEA) and 4-nitrosotoluene.[10] Methylbenzo[*c*]cinnoline-β-^{15}N was prepared from the 4-methylazobenzene-β-^{15}N by photochemical cyclodehydrogenation as described by Badger et al.[9]

Measurements. The ^{13}C NMR spectra were recorded on a JEOL FX-200 (50.2 MHz) spectrometer for neutral solutions and on a Varian CFT-20 (20.0 MHz) spectrometer for strong acid solutions. The spectra were taken under conditions of complete proton noise decoupling and at a pulse flip angle of 30–45° with 32K (FX-200) or 8K (CFT-20) of memory for 10 000–2000- (FX-200) or 4000–1000-Hz (CFT-20) spectral width. As neutral solutions, 0.3–0.8 mol dm^{-3} solutions of the azo compounds dissolved in $CDCl_3$ or $CCl_4-C_6D_{12}$ (10:1, v/v) were employed for the measurements. As strong acid solutions, 0.5–1.0 mol dm^{-3} solutions of the azo compounds dissolved in 16–22 N D_2SO_4–EtOH (7:1, v/v) were employed for the measurements. Chemical shifts were determined from internal

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TABLE I: Observed ^nJ(C-N) and $^{15}N/^{14}N$ Isotope Effects on ^{13}C Chemical Shifts of Azobenzene and Benzo[c]cinnoline

solvent	^nJ(C-N)[a] ^1J	^2J	isotope shift[b] C1($^{14}N_2$)-C1(^{14}N)	C1(^{14}N)-C1(^{15}N)	C1(^{15}N)-C1($^{15}N_2$)	C1($^{14}N_2$)-C1($^{15}N_2$)
			Azobenzene			
$CDCl_3$	+1.9	-5.3	0.005	0.010	0.003	0.018
$CCl_4 + C_6D_{12}$	+2.0	-5.6	0.004	0.012	0.002	0.018
22 N D_2SO_4 (+15% EtOH)	-7.1	-0.9	-0.025	0.075	-0.020	0.030
			Benzo[c]cinnoline			
$CDCl_3$	+7.3	+3.4	0.002	0.017	0.003	0.022
$CCl_4 + C_6D_{12}$	+8.3	+3.3	0.001	0.018	0.003	0.022
16 N D_2SO_4 (+10% EtOH)	-4.4	+3.7	-0.040	0.105	-0.045	0.020

[a] In Hz, ±0.1 Hz for neutral solutions and ±0.2 Hz for acidic solutions. [b] In ppm. A positive sign indicates an upfield ^{15}N isotope effect on a ^{13}C chemical shift; ±0.002 ppm for neutral solutions and ±0.01 ppm for acidic solutions. The assignments of C1(^{14}N) and C1(^{15}N) in benzo[c]cinnoline have been interchanged from those given in ref 6; see the text.

tetramethylsilane for the neutral solutions and from external dioxane (as 67.4 ppm) dissolved in D_2O, which was contained in a coaxial tube, for strong acid solutions. Digital resolutions for determination of isotope shifts were 0.1 Hz for the neutral solutions and 0.2 Hz for the strong acid solutions. Ambient probe temperatures were 34 °C for the neutral solutions and 35 °C for the strong acid solutions.

Results and Discussion

Isotope Shifts in Neutral Solutions. Figure 2 shows the ^{13}C NMR spectrum of the ipso (C1) carbons of *trans*-azobenzene. The sample was a mixture of the $^{14}N_2$, $^{15}N_1$, and $^{15}N_2$ compounds in $CDCl_3$. In this mixed spectrum, we can easily identify the origin of each signal because C1 in the $^{15}N_2$ compound appears as a triplet owing to its second-order spin system, whereas C1 in the $^{15}N_1$ compound appears as two sets of doublets owing to reduction to the first-order spin system by the ^{15}N monosubstitution. Each doublet arises from one- and two-bond ^{13}C–^{15}N spin–spin couplings.[6] The assignments thus identified are shown in the figures. Here, in addition to C1(^{14}N) and C1(^{15}N) in the $^{15}N_1$ compound, we represent the C1 carbons in $^{14}N_2$ and $^{15}N_2$ compounds as C1($^{14}N_2$) and C1($^{15}N_2$), respectively. Observed $^{15}N/^{14}N$ isotope shifts (δ_{IS}) are summarized in Table I together with the ^1J and ^2J values of the $^{15}N_1$ compounds; a positive sign of δ_{IS} indicates an upfield ^{15}N isotope effect on a ^{13}C chemical shift.

In the spectrum of *trans*-azobenzene, we can clearly see the following ordering: C1($^{14}N_2$), C1(^{14}N), C1(^{15}N), C1($^{15}N_2$) in order of increasing applied fields. This ordering is reasonable in the sense that a heavier isotopic substitution induced a high-field shift. Moreover, the relative magnitude of the isotope shifts among these carbons seems reasonable since δ_{IS} between C1($^{14}N_2$) and C1(^{15}N) or between C1(^{14}N) and C1($^{15}N_2$), which corresponds to α-isotope shift (0.015–0.013 ppm), is much larger than that between C1($^{14}N_2$) and C1(^{14}N) or between C1(^{15}N) and C1($^{15}N_2$), which corresponds to β-isotope shift (0.005–0.003 ppm). Interestingly, the magnitude of this α-isotope shift is smaller than those in cyano complexes ($C\equiv{}^{15}N$-, 0.03–0.04 ppm)[5a,b] and in pyrimidinetetrone (alloxan) oxime complexes ($C={}^{15}N-OH$, 0.025–0.030 ppm)[5c] in accord with the decreasing order of their carbon–nitrogen bond orders. On the other hand, in the mixed spectrum of benzo[c]cinnoline, the ordering observed was C1($^{14}N_2$), C1(^{15}N), C1(^{14}N), and C1($^{15}N_2$) from lowest to higher fields. As is to be expected, C1($^{14}N_2$) appeared at the lowest field and C1($^{15}N_2$) at the highest field. However, the ordering concerning C1(^{15}N) and C1(^{14}N) does not seem straightforward, because this ordering conflicts with our simple expectation that a heavier isotopic substitution would cause a high-field shift. The assignments for C1(^{15}N) and C1(^{14}N) were determined previously so as to satisfy the rule; that is, ^1J(C–N) which involves a nitrogen atom having an s-hybridized lone-pair orbital takes a small value because of the one-bond lone-pair effect.[7] For example, in quinoline, the values of ^1J(C2–N) and ^1J(C9–N) are 1.4 and 0.6 Hz, respectively.[11] Therefore, the C1 carbon which shows a splitting of 3.4 Hz can be assigned to C1(^{15}N) and the remaining carbon which shows a splitting of 7.3 Hz to C1(^{14}N). Here, even the value of 3.4 Hz seems too large for ^1J(C–N), much more the value of 7.3 Hz. In *trans*-azobenzene, ^1J(C–N) is 1.9 Hz, agreeing well with the rule. INDO-MO calculations predicted the increase of the ^1J values on transfer from *trans*-azobenzene (0.2 Hz) to benzo[c]cinnoline (4.7 Hz) or to *cis*-azobenzene (4.8 Hz);[6] however, it is of no service in assigning the ^1J and ^2J splittings convincingly.

Regarding the reversed order of chemical shifts of C1(^{15}N) and C1(^{14}N), we can consider two opposite possibilities: one is to accept this reversed order and the other is to deny the assignments and interchange them even though this latter procedure results in an abnormally large ^1J(C–N) value. Supporting evidence for the first view is given by the fact that many exceptions have been reported as to the high-field shift due to a heavier isotopic substitution.[12] Above all, the most interesting example is the cases found in *cis*- and *trans*-monodeuteriodifluoroethylene, CHF=CDF.[12a] In its cis isomer, the deuterium substitution causes a low-field shift to the remaining proton resonance, whereas in its trans isomer the deuterium substitution causes a high-field shift in conformity with a normal trend. This inversion of the direction of isotope shifts with the conformational change closely resembles our cases. However, of course, this example does not always mean that our first view is correct. On the other hand, we have no supporting evidence for the second view a priori. In overcoming these troublesome problems, the theoretical approach to verify either the conformational dependence of the direction of the isotope shift or the assignments for C1(^{15}N) and C1(^{14}N) is a difficult task. Thus, as a remaining approach, we aimed to assign C1(^{15}N) and C1(^{14}N) experimentally. To our best knowledge, however, there are no means to verify directly the assign-

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TABLE II: Observed ^{13}C Chemical Shifts and ^{n}J(C-N) of 4-Methylazobenzene-β-^{15}N and Methylbenzo[c]cinnoline-β-^{15}N in $CDCl_3$

4-methylazobenzene-β-^{15}N			methylbenzo[c]cinnoline-β-^{15}N		
carbons	δ(^{13}C)[a]	^{n}J(C-N)[b]	carbon	δ(^{13}C)[a]	^{n}J(C-N)[b]
1	150.8	$^{2}J = -5.4$	1	144.2	$^{2}J = +3.5$
2, 6	122.9	$^{3}J = -4.2$	2	130.9	$^{3}J = -3.3$
3, 5	129.7	$^{4}J < (0.6)$[c]	3	131.0	$^{4}J < (0.8)$[c]
4	141.4	$^{5}J = \pm 0.9$	4	142.2	$^{5}J = \pm 1.0$
1′	152.8	$^{1}J = +1.8$	5	120.5	$^{4}J < (0.8)$[c]
2′, 6′	122.7	$^{2}J = -3.9$	6	120.7	$^{3}J = -0.9$
3′, 5′	129.0	$^{3}J = \pm 2.0$	1′	145.3	$^{1}J = +7.2$
4′	130.6	$^{4}J = \pm 0.7$	2′	131.0	$^{2}J = -9.7$
			3′	128.9	$^{3}J = \pm 3.5$
			4′	131.1	$^{4}J = \pm 0.9$
			5′	121.3	$^{3}J < (0.8)$[c]
			6′	120.8	$^{2}J = +4.5$

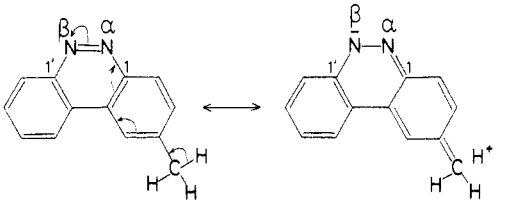
[a] In ppm from Me_4Si, ± 0.1 ppm. [b] In Hz, ± 0.1 Hz. Signs are taken from those of ^{n}J(C-N) of neutral solutions of azobenzene-^{15}N and benzo[c]cinnoline-^{15}N (see ref 6). [c] Unresolved. Half-height line width is shown here.

ments for the two C1 carbons in benzo[c]cinnoline-^{15}N itself. Thus, as the second best method, we have tried to observe the ^{13}C–^{15}N spin-coupling constants of substituted benzo[c]cinnoline. In the substituted benzo[c]cinnoline, if we can obtain the least modified compound of it, the magnitudes of its ^{13}C–^{15}N coupling constants would be expected to be almost identical with the corresponding coupling constants of benzo[c]cinnoline; thus, the assignments can be determined. As the most suitable compound we have chosen methyl-substituted benzo[c]cinnoline and synthesized its ^{15}N-enriched material at the β position. Observed spin-coupling constants in $CDCl_3$ solutions are summarized in Table II. For reference purposes we have also observed spin-coupling constants of 4-methylazobenzene-β-^{15}N. In order to afford unambiguous assignments for the ^{13}C resonances, we performed selective ^{13}C–[^{1}H] decouplings. The ^{1}H NMR spectra were assigned by NOE difference and homonuclear decoupling experiments starting from the CH_3 protons.

Observed ^{n}J(C-N) values of 4-methylazobenzene agreed well with those of azobenzene within the experimental error. This result supports "experimentally" our previous assignments for the pairs of coupling constants, ^{n}J(C-N) and ^{n+1}J(C-N), of azobenzene.[6] Similarly, the ^{n}J(C-N) values of methylbenzo[c]cinnoline, except ^{1}J and ^{2}J, agreed well with those of benzo[c]cinnoline. In the methylbenzo[c]cinnoline, the C1′ carbon showed a splitting of 7.2 Hz, while the C1 carbon showed a splitting of 3.5 Hz. Since N_β is ^{15}N enriched, the former splitting undoubtedly arises from ^{13}C–^{15}N one-bond coupling (^{1}J) and the latter from two-bond coupling (^{2}J). This finding means that our previous assignments for the two C1 carbons, C1(^{15}N) and C1(^{14}N), in benzo[c]cinnoline-^{15}N are erroneous and thus they should be interchanged.

The reason for the large ^{1}J(C-N) in benzo[c]cinnoline seems to arise from the cis configuration of its two lone pairs. On the basis of semiempirical coupled Hartree–Fock perturbation theory, Schulman et al. showed that the N–N one-bond coupling constant in hydrazine greatly depends on mutual arrangements of the two lone pairs.[13] They also showed that contributions to the Fermi contact term from the lone-pair orbitals are large and negative in the case of cis arrangement and positive in the case of trans arrangement. If the C–N coupling in the CN=NC group depends likewise on the dihedral angle around the N=N bond, it would be expected that ^{1}J(C-N) would be positive in sign (since $\gamma_C\gamma_N < 0$) and larger than that which would be expected by considering the one-bond lone-pair effect, as observed. A similar reasoning can be expected to hold for *cis*-azobenzene; then, the assignments for C1(^{15}N) and C1(^{14}N) of *cis*-azobenzene have also to be interchanged.[14]

Isotope Shifts in Strong Acid Solutions. Observed isotope shifts of *trans*-azobenzene and benzo[c]cinnoline in strong acid media are shown in Table I. In benzo[c]-cinnoline-^{15}N, the assignments for C1(^{14}N) and C1(^{15}N) have also been interchanged from those given previously by considering ^{1}J(C1–N) and ^{2}J(C1–N) of methyl-substituted benzo[c]cinnoline. In Table III we listed observed ^{n}J(C–N) (n = 1–3) values of methylbenzo[c]cinnoline-β-^{15}N and 4-methylazobenzene-β-^{15}N.[15] In contrast with the cases of neutral solutions, these values do not always exactly coincide with those of the corresponding parent molecules. This is because the methyl substitution causes N_β to be more basic than N_α as will be realized, for example, from the following resonance structure with methylbenzo[c]cinnoline:



This was, in fact, reflected in a greater higher-field shift of C1′ than C1; the high-field shift upon protonation was well investigated previously.[16] Thus, for example, ^{1}J(C1′–N_β) would be expected to become more negative than that of the corresponding parent molecule since the enhanced protonation on the N_β eliminates the one-bond lone-pair effect[7] more effectively than that on the azo nitrogens of the parent molecule. Indeed, the ^{1}J value of 4-methylazobenzene (–10.6 Hz) is more negative than that of azobenzene (–7.1 Hz). Interchange of the assignments between C1(^{14}N) and C1(^{15}N) of benzo[c]cinnoline-^{15}N results in $^{1}J = -4.4$ and $^{2}J = +3.7$ Hz, agreeing well with ^{1}J (=–6.3 Hz) and ^{2}J (=+3.6 Hz) of methylbenzo[c]-cinnoline.

The ordering of chemical shifts observed is surprising because it was C1(^{14}N), C1($^{14}N_2$), C1($^{15}N_2$), and C1(^{15}N) but not the expected order of C1($^{14}N_2$), C1(^{14}N), C1(^{15}N), and C1($^{15}N_2$) from lowest to higher fields. As mentioned before, δ_{IS}'s between C1(^{14}N) and C1(^{15}N) of *trans*-azobenzene and benzo[c]cinnoline increased greatly compared with those in the $CDCl_3$ solutions. Interestingly, however, δ_{IS}'s between C1($^{14}N_2$) and C1($^{15}N_2$) of both compounds, which correspond to the sum of α- and β-isotope shifts, are of comparable magnitudes to those in the $CDCl_3$ solutions. These findings mean that a mechanism of the isotope effect acting on the ^{13}C chemical shifts of $^{15}N_1$ compounds is different from that acting on those of $^{15}N_2/^{14}N_2$ compounds, the mechanism for the latter probably being the

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(14) Consequently, in ref 6, the absolute magnitudes of ^{1}J and ^{2}J in benzo[c]cinnoline and in *cis*-azobenzene (Tables I–III and V in ref 6) have to be interchanged retaining each sign as it is, e.g., (^{1}J, ^{2}J) = (+3.9, +10.0) in *cis*-azobenzene have to be changed to (^{1}J, ^{2}J) = (+10.0, +3.9). In addition, in Table IV, all the positive signs have to be changed to negative signs.

(15) Here, the assignments of the ^{13}C resonances were determined by selective ^{13}C–[^{1}H] decouplings and/or by varying the acidity of the solution stepwise.

(16) Kuroda, Y.; Kuwae, A.; Fujiwara, Y. *Chem. Pharm. Bull.* **1982**, *30*, 2667–72.

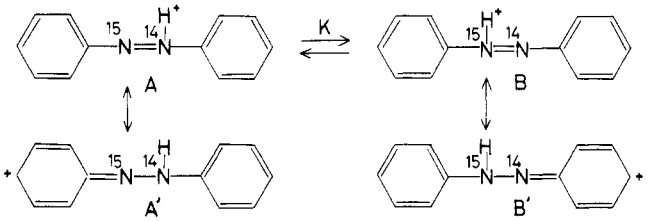
TABLE III: Observed ^{13}C Chemical Shifts and $^{n}J(C-N)$ (n = 1-3) of 4-Methylazobenzene-β-^{15}N and Methylbenzo[c]cinnoline-β-^{15}N in Strong Acid Media

4-methylazobenzene-β-^{15}N			methylbenzo[c]cinnoline-β-^{15}N		
carbons	$\delta(^{13}C)^a$	$^{n}J(C-N)^b$	carbon	$\delta(^{13}C)^a$	$^{n}J(C-N)^b$
1	142.6	$^{2}J < (1.0)^{c,d}$	1	140.2	$^{2}J = +3.6\ (+3.6)^c$
2, 6	127.8	$^{3}J = -4.0^c$	2	128.8	$^{3}J = -3.1^c$
1′	142.4	$^{1}J = -10.6\ (-10.3)^c$	6	127.2	$^{3}J = -4.2\ (-4.2)^c$
2′, 6′	125.0	$^{2}J = -2.4^c$	1′	139.2	$^{1}J = -6.3\ (-6.3)^c$
			2′	125.6	$^{2}J = -5.2^c$
			6′	126.6	$^{2}J = +0.3^c$

[a] In ppm from external dioxane (67.4 ppm), ±0.1 ppm. [b] In Hz, ±0.2 Hz. Signs are taken from those of $^{n}J(C-N)$ of acidic solutions of azobenzene and benzo[c]cinnoline (see ref 6). [c] Observed at 55 °C. [d] Unresolved. Half-height line width is shown here.

same as that in the $CDCl_3$ solutions.

In general, mechanisms of isotope effects on NMR chemical shifts can be divided broadly into two categories: one is an intrinsic isotope effect[4g] and the other is an equilibrium isotope effect.[4f] Although both isotope effects are attributable to the difference in the amplitudes of zero-point vibrations between the isotopes, the vibrational potential energy surface is single minimum for the former intrinsic isotope effect and double minimum for the latter equilibrium isotope effect. Thus, the magnitude of the intrinsic isotope shift is usually smaller than that of the equilibrium isotope shift. In the $CDCl_3$ solutions of the present azo compounds, no equilibrium process except for hydrogen bonding between the $CDCl_3$ and the azo nitrogens is expected. This hydrogen bonding is expected to affect the chemical shifts of the C1 carbon since the strength of the hydrogen bonding may differ more or less between ^{14}N and ^{15}N. However, as shown in Table I, observed isotope shifts in CCl_4–C_6D_{12} solutions agreed very closely with those in the $CDCl_3$ solutions. Therefore, all the isotope shifts observed in $CDCl_3$ solutions can be regarded as the intrinsic isotope shifts. On the other hand, in strong acid solutions, there exist interesting protonation equilibria between ^{14}N and ^{15}N atoms of $^{15}N_1$ compounds. For example, with azobenzene-^{15}N, the following protonation equilibrium (A ⇄ B) can be considered:



If the protonation occurs preferentially on either ^{14}N (A) or ^{15}N (B), then δ_{IS} between C1(^{14}N) and C1(^{15}N) would become much larger than that in the $CDCl_3$ solution since the protonation enables such a resonance structure as A′ or B′ which leads to a large chemical shift separation between the C1 carbon attached to the protonated nitrogen, C1(NH), and that attached to the unprotonated nitrogen, C1(N). Regarding $^{14}N_2$ and $^{15}N_2$ compounds, this protonation is "degenerate" on the two identical nitrogens; thus, it causes no chemical shift separation within themselves. Consequently, the mechanism of isotope shifts in the $^{15}N_1$ compounds can be termed an "isotopic perturbation of a degenerate protonation equilibrium". In the symmetrical $^{14}N_2$ and $^{15}N_2$ compounds, it is hardly expected that a small difference in the extent of protonation arising from a small difference in pK_a between ^{14}N and ^{15}N would cause an observable extent of isotope shift. Thus, δ_{IS} between C1($^{14}N_2$) and C1($^{15}N_2$) in strong acid solutions can also be ascribed to the intrinsic isotope shifts. This is the reason that they are almost identical with the corresponding values in the neutral solutions.

TABLE IV: Δ and δ Values, Calculated Equilibrium Constants (K), and pK_a Difference ($\Delta(pK_a)$) between ^{15}N and ^{14}N of Azobenzene-^{15}N and Benzo[c]cinnoline-^{15}N

acid	Δ^a	$\Delta(cor)^{a,b}$	δ^a	K	$\Delta(pK_a)^c$
		Azobenzene-^{15}N			
D_2SO_4	−2.20	−2.49	0.065	1.054	0.0228
H_2SO_4	−2.08	−2.35	0.055	1.048	0.0204
		Benzo[c]cinnoline-^{15}N			
D_2SO_4	−2.11	−4.03	0.088	1.045	0.0191
H_2SO_4	−1.96	−3.73	0.073	1.040	0.0170

[a] In ppm, ±0.01 ppm. [b] Corrected by taking into account the extent of protonation; see the text. [c] $\Delta(pK_a) = pK_a(^{15}N) - pK_a(^{14}N)$.

In the $^{15}N_1$ compounds, an equilibrium constant, K, for the A ⇄ B protonation equilibrium can be calculated from the following equation:[4f]

$$K = B/A = (\Delta - \delta)/(\Delta + \delta)$$

where Δ is the chemical shift difference between C1(NH) and C1(N) in the "frozen" protonation equilibrium and δ is the difference between δ_{IS} in a strong acid solution (i.e., an isotope shift due to the protonation equilibrium including an intrinsic isotope shift) and that in a $CDCl_3$ solution (i.e., an intrinsic isotope shift).[17] Since the Δ values for *trans*-azobenzene and benzo[c]cinnoline cannot be determined easily, they were estimated from 4-methylazobenzene and methylbenzo[c]cinnoline, respectively. In practice, Δ was then defined as the difference of protonation shifts between C1′ and C1 in the methyl-substituted compounds.[18] Moreover, since the $^{1}J(C-N)$ values of 4-methylazobenzene (−10.6 Hz) and methylbenzo[c]cinnoline (−6.3 Hz) do not seem to be the ones of fully protonated nitrogens, we corrected the difference of the protonation shifts by considering that a $^{1}J(C-N)$ value including the fully protonated nitrogen takes a value of −12.0 Hz. This value is a typical magnitude for the one-bond coupling constant released from the suppression of the one-bond lone-pair effect, and was taken from $^{1}J(C1-N_\alpha)$ of N_α- and amino-protonated 4-aminoazobenzene.[19] The Δ and δ values of azobenzene and benzo[c]cinnoline and calculated K values are listed in Table IV. Since logarithms of the K values correspond to the pK_a difference ($\Delta(pK_a)$) between ^{15}N and ^{14}N atoms, they are also shown in Table IV. In addition, since all the acids so far used in the present experiments were D_2SO_4 (for locking purposes of the magnetic fields), we have also tried to observe $^{2}H/^{1}H$ isotope effects on Δ and δ using H_2SO_4 as a source

(17) δ = [δ(C1(^{14}N)) − δ(C1(^{15}N))] − (intrinsic isotope shift) = [{$A\delta$(C1(NH)) + $B\delta$(C1(N))} − {$A\delta$(C1(N)) + $B\delta$(C1(NH))}]/(A + B) = Δ(A − B)/(A + B), where Δ = δ(C1(NH)) − δ(C1(N)).

(18) Δ = [δ(C1′(acid)) − δ(C1′ (neutral))] − [δ(C1(acid)) − δ(C1(neutral))].

(19) Kuroda, Y.; Lee, H.; Kuwae, A. *J. Phys. Chem.* **1980**, *84*, 3417–23.

of the "proton".[20] As can be seen from Table IV, this $^2H/^1H$ isotope effect on δ is almost negligible but on Δ is significant and, as a consequence of this, K and $\Delta(pK_a)$ become smaller in the H_2SO_4 solutions than those in the D_2SO_4 solutions. Interestingly, the calculated K values of both azobenzene and benzo[c]cinnoline are approximately equal to 1.05. This result means that the protonation equilibria in the $^{15}N_1$ compounds are displaced to the ^{15}N protonation and that to the same extent regardless of the large difference in pK_a values between *trans*-azobenzene ($pK_a = -2.95$)[21] and benzo[c]cinnoline ($pK_a = +2.10$).[22] Thus, it is concluded that the large isotope shifts observed in the strong acid solutions of the $^{15}N_1$ compounds were caused by the pK_a difference between ^{15}N and ^{14}N atoms, the former being more basic by about 0.02 pK_a unit.

Acknowledgment. We thank Professor M. Okamoto of the Kyoto College of Pharmacy for providing facilities to synthesize the materials.

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Photochemical Preparation and Identification of *cis,cis*-1,3,5,7-Octatetraene

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Irradiation of a 10 K solid solution of 10^{-3} M cyclooctatriene in *n*-octane with 301-nm light generates a tetraene which is neither all-trans octatetraene nor mono-cis octatetraene. This thermally labile, centrosymmetric molecule is identified as *cis,cis*-1,3,5,7-octatetraene.

Introduction

The electronic structure and photochemical behavior of linear polyenes are of considerable interest. This interest is motivated both by the conceptual simplicity of these linear π-electron systems and the fact that an understanding of electronic structure in the simple unsubstituted polyenes is key to developing models for such diverse phenonoma as transport in polyacetylene and visual transduction. In the particular case of visual transduction, the role of the cis to trans photoisomerization of the polyene chromophore retinal is currently at issue.[1] Unfortunately, because of inhomogeneous broadening,[2] the electronic absorption and emission spectra of retinal contain no resolved vibrational structure. Thus, no direct experimental information on the coupling between electronic excitation and photoisomerization can be determined from retinal optical spectra. However, it is possible to prepare and study simpler model polyenes where the mechanism for inhomogeneous broadening that is operative in retinal is missing. 1,3,5,7-Octatetraene in an *n*-alkane host maintained at liquid helium temperatures exhibits well-resolved spectra[3,4] and is photochemically active.[5] Of the three possible double bond isomers, only the all-trans and mono-cis species have been unambiguously identified and studied under high-resolution conditions.[4,5] The third isomer, *cis,cis*-octatetraene, is not stable in room temperature solutions[6] and has not yet been prepared in sufficient quantity and purity for detailed spectroscopic study. Data, Goldfarb, and Boikes[7] reported that the photolysis of 1,3,5-cyclooctratriene in a low-temperature matrix results in the formation of several octatetraene isomers, one of which they argued must have been *cis,cis*-octatetraene. Positive identification was not possible because of the complexity of the sample and the resulting congestion in the IR spectrum. In *n*-alkane matrixes the optical spectra of octatetraene isomers are sufficiently resolved that it is easy to unambiguously distinguish between the π isomers. In this paper we report the photochemical preparation and spectroscopic identification of *cis,cis*-octatetraene.

Experimental Section

Cyclooctatriene was purchased from Orgmet Chemical Co. Gas chromatographic analysis established that the purity was >98%. *n*-Octane was purchased from Wiley Organics and further purified by passage over a $AgNO_3$–alumina column. Samples of cyclooctatriene approximately 10^{-3} M in *n*-octane were contained in 2-μL capillary cells. These cells were mounted in a CTI closed-cycle helium refrigerator modified to allow an atmosphere of hydrogen or helium gas to surround the cold stage and the sample capillary, thus ensuring good thermal contact. Photolysis of the cyclooctatriene samples was effected by 30–50 mW of 301-nm light having a bandwidth of 8 nm derived from a 100-W Hg lamp dispersed through a Jobin-Yvon 0.2-m double monochromator. The apparatus used to measure the excitation and emission spectra has been described previously.[4] Emission spectra were measured with a Jobin-Yvon 1.5-m monochromator by using standard techniques.

Results and Discussion

No emission from cyclooctatriene could be detected under the conditions of our experiments. However, pho-

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