Determination of the Sign of a One-bond ^{15}N–^{15}N Spin–Spin Coupling Constant for a *trans*-Diazene by Selective ^{15}N Decoupling Experiments in ^{13}C Nuclear Magnetic Resonance Spectroscopy

Yoshihiro Kuroda *
Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, Japan
Yasuhiro Fujiwara
Kyoto Pharmaceutical University, Yamashina-ku, Kyoto 607, Japan
Akio Kuwae
College of General Education, Nagoya City University, Mizuho-ku, Nagoya 467, Japan
Kazuhiro Matsushita
NMR Application Laboratory, JEOL Ltd., Akishima, Tokyo 196, Japan

The sign of the one-bond ^{15}N–^{15}N spin–spin coupling constant, ^1J(N–N), of a *trans*-diazene (4-acetylaminoazobenzene) has been determined to test the theoretical prediction that ^1J(N–N) would be positive in sign when nitrogens have *s*-hybridized lone pairs and take a *trans* conformation. The sign was first determined relative to those of ^{13}C–^{15}N spin–spin coupling constants, ^nJ(C–N), by selective ^{15}N decoupling experiments and then finally referenced to that of ^1J(C–H) in the benzene ring, which undoubtedly bears a positive sign, by selective ^{15}N and ^1H decoupling experiments. It was found that the sign of ^1J(N–N) of the *trans*-diazene is negative in contrast to the theoretical prediction. This discrepancy is attributed to the large negative contribution from the orbital–dipole term which was not correctly evaluated in previous calculations for the ^1J(N–N) coupling of the N=N bond.

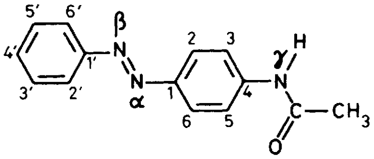

Figure 1. Structure and numbering scheme of 4-acetylaminoazobenzene (acetylAAB)

Lone pair electrons of a nitrogen nucleus have been shown to affect signs and magnitudes of spin–spin coupling constants which involve the nitrogen nucleus. This situation is demonstrated by both experiment and theory for the two-bond ^{15}N–^1H and ^{13}C–^{15}N couplings and one-bond ^{13}C–^{15}N couplings.[1,2] Regarding a one-bond ^{15}N–^{15}N coupling, Schulman *et al.* have calculated ^1J(N–N) in hydrazine as a function of lone pair character and dihedral angle by using INDO[3] and *ab initio*[4] coupled Hartree–Fock perturbation theory. One of the most interesting findings in their calculations is that the ^1J(N–N) strongly depends on the dihedral angle when both nitrogen nuclei possess *s*-hybridized lone pairs. Their calculations showed that ^1J(N–N) is negative when the lone pair orbitals are *syn*, while it is positive when they are *anti*. The same sort of sign reversal is also expected between *cis*- and *trans*-diazenes.[3] In fact, our calculations on ^1J(N–N) of 3-methylpyridazine[5] and *trans*-4-aminoazobenzene[6] at the INDO MO level of approximation predicted negative and positive signs, respectively. Previously, we confirmed experimentally that ^1J(N–N) of 3-methylpyridazine is undoubtedly negative in sign as predicted by theory.[5] However, no experimental sign determination has yet been made for *trans*-diazenes. This work was undertaken to determine the sign of ^1J(N–N) of *trans*-diazenes (Figure 1). The strategy adopted is to determine the sign of ^1J(N–N) relative to that of ^2J[C(1)–N(β)] or ^2J[C(1′)–N(α)] by selective ^{15}N decoupling experiments in ^{13}C n.m.r. spectroscopy, since these two-bond ^{13}C–^{15}N couplings should undoubtedly be negative in sign from considerations of lone pair orientation.

In order that this strategy succeed fully, one-bond ^{13}C–^{15}N couplings ^1J[C(1)–N(α)] and/or ^1J[C(1′)–N(β)] should be well resolved signals in an unsymmetrical *trans*-diazene [*i.e.*, ^1J(N–N) should be observed in the present method]. Unfortunately, in *trans*-diazenes, the absolute magnitude of ^1J(C–N) is usually small or nearly zero on account of the one-bond lone-pair effect.[7] For example, [$^{15}N_3$]-4-aminoazobenzene dissolved in [$^2H_6$]dimethyl sulphoxide showed no splitting due to the ^1J(C–N).[6] However, amino-protonated [$^{15}N_3$]-4-aminoazobenzene (+1.1 Hz)[6] and [$^{15}N_2$]azobenzene (+1.9 Hz)[8,9] show a definite splitting due to ^1J(C–N). In these molecules, a resonance structure which makes the molecule planar cannot be expected in contrast to the case of 4-aminoazobenzene; hence, the increased *s*-character of N(α) and/or N(β) on account of the decreased steric interference from *ortho*-hydrogens of the benzene ring can be considered to be responsible for the difference in the magnitude of ^1J[C(1)–N] between 4-aminoazobenzene and its protonated form or azobenzene. For this reason, 4-acetylaminoazobenzene (acetylAAB; Figure 1) was chosen in the present work and its ^{15}N-enriched material ([$^{15}N_3$]acetylAAB) was synthesized. As will be described, since the sign of ^1J(N–N) was found to be negative in contrast to the theoretical prediction, we further tried to refer the sign of ^1J(N–N) to that of ^1J[C(2),(6)–H(2),(6)] of the aminobenzene ring by way of those of ^2J[C(2),(6)–N(α)] and ^3J[N(α)–H(2),(6)]. For this purpose, [^{15}N]-4-aminoazobenzene [enriched at N(α)] was also employed. This trial confirmed that ^1J(N–N) is negative in sign.

Experimental

Materials.—[$^{15}N_3$]-4-Acetylaminoazobenzene ([$^{15}N_3$]-acetylAAB)[10] was prepared in the usual way by treating [$^{15}N_3$]-4-aminoazobenzene ([$^{15}N_3$]AAB) with acetic anhydride in pyridine. [$^{15}N_3$]AAB was synthesized from [^{15}N]aniline (95% enriched; Hikari Kogyo, Tokyo) and sodium [^{15}N]nitrite (97.5% enriched; CEA).[11] [α-^{15}N]-4-Aminoazobenzene

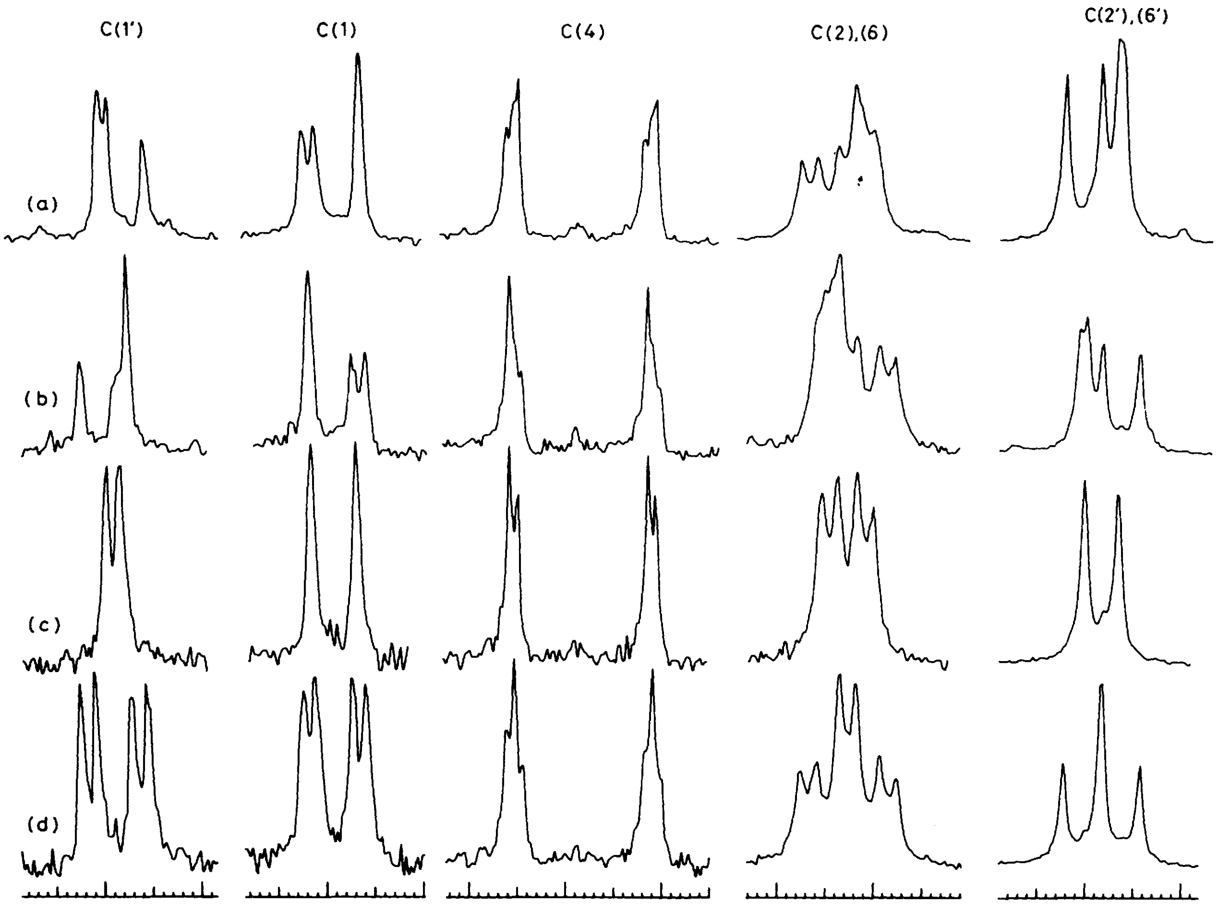

Figure 2. Complete proton noise-decoupled ^{13}C n.m.r. spectra of C(1'), C(1), C(4), C(2),(6), and C(2'),(6') of [$^{15}N_3$]acetylAAB in [$^2H_6$]dimethyl sulphoxide: (a) with selective ^{15}N irradiation at a frequency shifted by 8 Hz from the N(α) chemical shift to lower field; (b) as in (a), but shifted by 8 Hz to higher field; (c) with selective ^{15}N irradiation at the N(α) chemical shift; (d) with no ^{15}N irradiation. The ^{15}N irradiation power was *ca.* 0.18 mW in (a) and (b), and 18 mW in (c). Digital resolution was 0.24 Hz per point. One division is equal to 1 Hz

([^{15}N]AAB) was prepared from ordinary aniline and sodium [^{15}N]nitrite.

Measurements.—The ^1H (199.6 MHz), ^{13}C (50.2 MHz), and ^{15}N (20.2 MHz) n.m.r. spectra were recorded on a JEOL FX-200 spectrometer. Selective ^{15}N decoupling experiments were performed by the method described elsewhere.[12] Ambient probe temperature was maintained at 45.2 ± 0.3 °C. Samples were dissolved in [$^2H_6$]dimethyl sulphoxide ([$^{15}N_3$]acetylAAB, 1.7 mol dm^{-3}) or in $CDCl_3$ ([^{15}N]AAB, 1.5 mol dm^{-3}). The chemical shifts of the ^1H and ^{13}C resonances were referenced to internal tetramethylsilane and those of ^{15}N to external neat liquid nitromethane which was contained in an inner co-axial tube.

Results

Figure 2 shows complete proton noise-decoupled ^{13}C n.m.r. spectra of C(1'), C(1), C(4), C(2),(6), and C(2'),(6') in [$^{15}N_3$]acetylAAB with (a—c) and without (d) selective ^{15}N irradiation. Figure 2(c) was obtained by applying relatively strong ^{15}N irradiation power (18 mW) at the N(α) chemical shift, while Figures 2(a) and (b) were obtained by applying much weaker ^{15}N irradiation power (0.18 mW) at frequencies which were shifted by 8 Hz from the N(α) chemical shift to low and high field, respectively. The corresponding ^{13}C n.m.r. spectra which were irradiated selectively at the freqencies of N(β) resonances are shown in Figure 3. ^{13}C N.m.r. spectra for the other carbons are omitted here, since they showed no appreciable changes in their spectral patterns between the spectra recorded by applying the ^{15}N irradiation power to the low or high field from the N(α) or N(β) chemical shift. The ^{13}C–^{15}N spin–spin coupling constants, ^nJ(C–N), and the ^{13}C chemical shifts of the ring carbons are summarized in the Table. The ^{13}C resonances were assigned by taking into account the corresponding ones of 4-aminoazobenzene in [$^2H_6$]dimethyl sulphoxide[6] and also by considering the magnitudes of ^nJ(C–N). The spin-coupling assignments were unequivocally made by selective ^{15}N decoupling experiments for N(α) (126.1), N(β) (119.6), and N(γ) (−243.6 p.p.m.) resonances. The N(α) and N(β) resonances were clearly differentiated by comparing the ^{15}N spectrum with that of [α-^{15}N]-4-acetylaminoazobenzene in [$^2H_6$]dimethyl sulphoxide. The ^{15}N(α)–^{15}N(β) one-bond coupling constant, the sign of which is to be determined, was 15.6 ± 0.1 Hz. The magnitudes of these ^nJ(C–N) and ^1J(N–N) correspond well with those of 4-aminoazobenzene,[6] except that ^1J[C(1)–N(α)] and ^1J[C(1')–N(β)] could be observed as well resolved signals, as expected from the decreased electron-donating ability of the substituent by *N*-acetylation which prevents formation of a planar structure. Long-range couplings between C(4) and N(α) (^4J) or N(β) (^5J) could also be newly detected; this might be due to the increased digital resolution compared with our previous condition.

Figure 4 shows the schematic diagrams for ^{15}N and ^{13}C at a complete proton noise-decoupled state; the diagrams are not

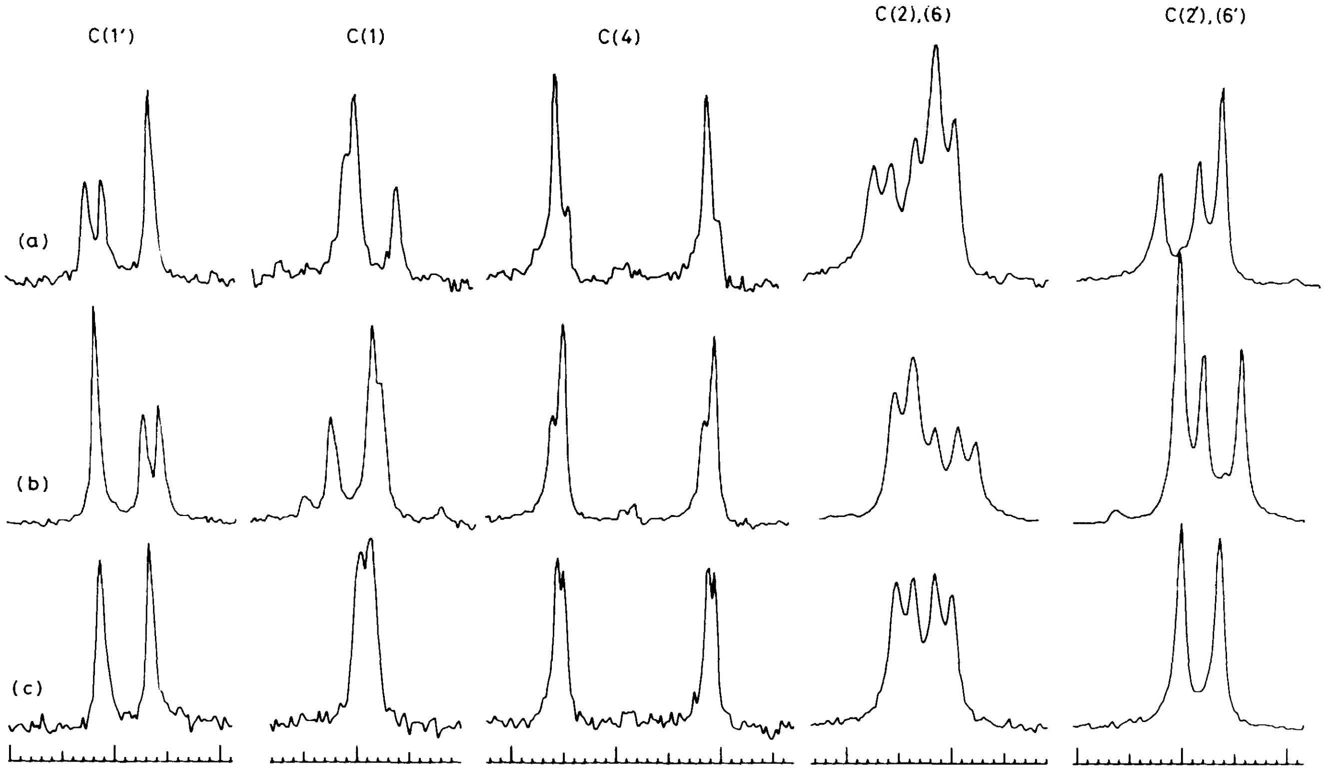

Figure 3. ^{13}C N.m.r. spectra which correspond to Figures 2(a)—(c), respectively, but irradiated at the N(β) resonance frequencies. One division is equal to 1 Hz

Table. Observed ^{13}C–^{15}N spin–spin coupling constants, ^{n}J(C–N), their signs, and ^{13}C chemical shifts of the ring carbons of [$^{15}N_3$]-4-acetylaminoazobenzene ([$^{15}N_3$]acetylAAB) in [$^{2}H_6$]dimethyl sulphoxide at 45 °C

n	C[a]	N[a]	^{n}J(C–N)[b]	Sign	Chemical shifts[c]
1	4	γ	14.4		142.4
2	3,5	γ	1.7		119.2
3	2,6	γ	1.7		123.5
1	1	α	1.2	+	147.5
2	1′	α	5.1	−	152.2
2	2,6	α	4.2	−	
3	3,5	α	1.7		
3	2′,6′	α	3.9	−	122.3
4	4	α	0.7	+	
1	1′	β	1.5	+	
2	1	β	5.1	−	
2	2′,6′	β	3.9	−	
3	3′,5′	β	1.7		129.3
3	2,6	β	4.2	−	
4	4′	β	0.5		130.8
5	4	β	0.7	−	

[a] The numbering scheme is shown in Figure 1. [b] In Hz, ±0.2 Hz. [c] In p.p.m. from internal Me$_4$Si, ±0.1 p.p.m.

always drawn to scale. For illustrative purposes, ^{15}N spin states are distinguished by plus and minus signs; the convention is that the plus sign at a higher field (*i.e.* lower frequency) signal denotes a positive 'reduced' coupling constant, ^{n}K.[13] The ^{n}K does not depend on the sign of the magnetogyric ratios involved in the spin–spin coupling. Thus, the positive sign at a higher field signal means negative and positive signs of *J*(C–N) and *J*(N–N), respectively. The ^{15}N spin states indicated in Figure 4 are so written as to satisfy the observations in Figures 2 and 3, as will be discussed in the following.

As shown in Figure 2(d), the ^{13}C n.m.r. spectrum of C(1) appeared as a doublet (5.1 Hz) of doublets (1.2 Hz). The larger splitting corresponds to ^{2}J[C(1)–N(β)] and the smaller one to ^{1}J[C(1)–N(α)]; this assignment is unambiguous because selective irradiation of N(α) transitions left the larger splitting [Figure 2(c)], while that of N(β) the smaller one [Figure 3(c)]. Selective irradiation at frequencies somewhat to high [Figure 2(b)] or low field [Figure 2(a)] from the N(α) chemical shift effectively decoupled the low and high field splittings due to ^{1}J[C(1)–N(α)], respectively. These observations clearly indicate that the spin states of N(β) in N(α) and C(1) can be written as shown in Figure 4. Thus, ^{1}K(N–N) and ^{2}K[C(1)–N(β)] have opposite signs to each other. Since the sign of ^{2}J[C(1)–N(β)] is considered to be negative by taking into account the lone pair orientation on N(β) relative to C(1), ^{1}J(N–N) can be considered to be negative in sign. This result is in clear contrast to our expectation that it would be positive as implied by theoretical calculations.[3,4,6] We can reach the same conclusion from the ^{13}C n.m.r. spectra of C(1′) in Figures 3(a) and (b) [see also schematic diagrams for N(β) and C(1′)], *i.e.*, ^{1}K(N–N) and ^{2}K[C(1′)–N(α)] are of different signs. Comparison of the changes in the spectral patterns between Figures 2(a) and (b) and between 3(a) and (b) with relevant schematic diagrams in Figure 4 also gives relative signs between the other ^{n}J(C–N) and ^{1}J(N–N). These results are indicated in the Table, where caution should be paid that all the absolute signs are based on negative signs of ^{2}J[C(1)–N(β)] and ^{2}J[C(1′)–N(α)]. It is interesting to note that the present method of sign determination could give signs of long-range ^{13}C–^{15}N couplings in C(4). Sign alternations on going from $^{3}J(-)$ to $^{4}J(+)$ and $^{5}J(-)$ correspond well with those found for ^{13}C–^{13}C couplings in aromatic systems,[14] indicating the dominant π-electron

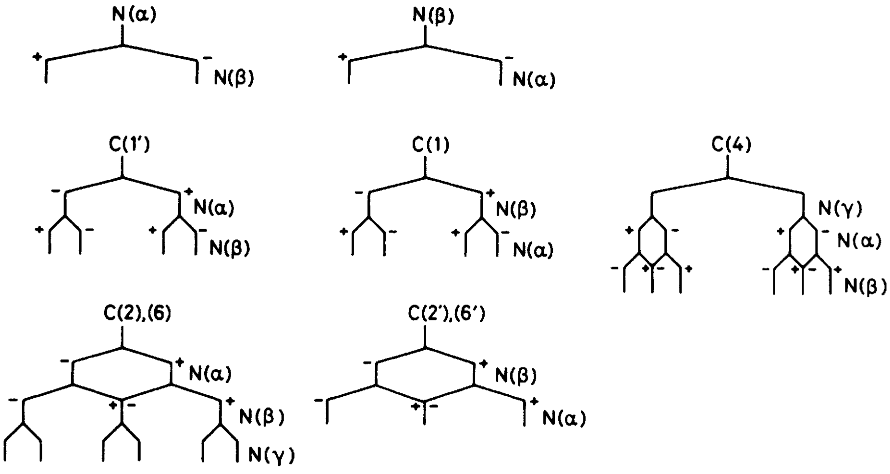

Figure 4. Schematic diagrams for ^{15}N and ^{13}C nuclei observed at a complete proton noise-decoupled state. ^{1}J[N(α)–N(β)] = 15.6 ± 0.1 Hz and the magnitudes of ^{n}J(C–N) are shown in the Table

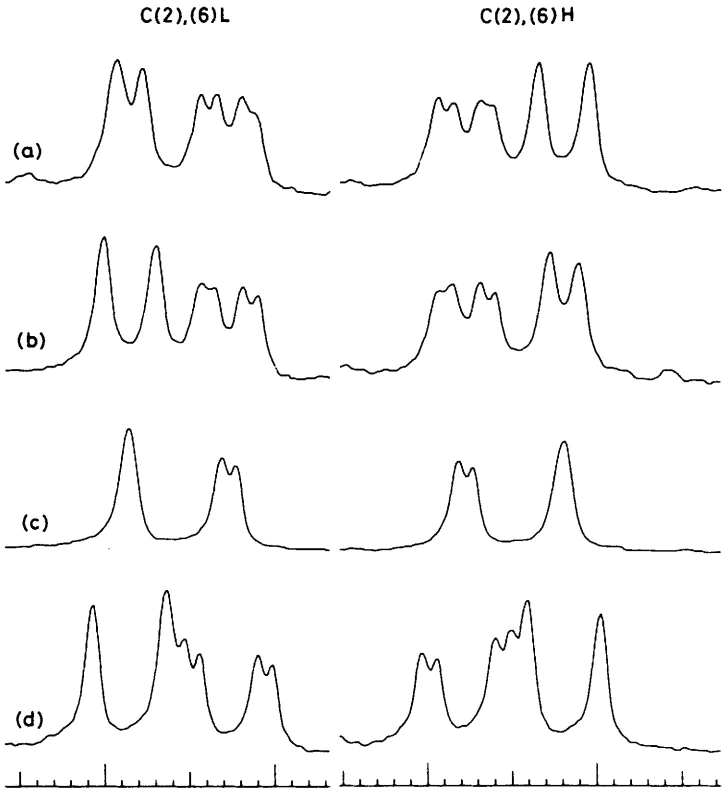

Figure 5. Proton-coupled ^{13}C n.m.r. spectra of C(2),(6) (125.1 p.p.m.) of [^{15}N]AAB in CDCl$_3$: (a) with selective ^{15}N irradiation at a frequency shifted by 4 Hz from the N(α) chemical shift (121.7 p.p.m.) to lower field; (b) as in (a), but shifted by 4 Hz to higher field; (c) with selective ^{15}N irradiation at the N(α) chemical shift; (d) with no ^{15}N irradiation. In practice, all these spectra were obtained as a gated mode of operation to enhance signals by the nuclear Overhauser effect. The low- and high-field components of C(2),(6), which were separated by one-bond ^{1}J[C(2),(6)–H(2),(6)] coupling, are denoted as C(2),(6)L and C(2),(6)H, respectively. The ^{15}N irradiation power was *ca.* 0.20 mW in (a) and (b), and 1.5 mW in (c). Digital resolution was 0.30 Hz per point. One division is equal to 1 Hz

contribution to these long-range ^{13}C–^{15}N couplings; hence, their absolute signs seem reasonable. More importantly, the currently obtained signs of the ^{13}C–^{15}N couplings in ^{1}J, ^{2}J, and ^{3}J agree with those of the corresponding couplings in *trans*-azobenzene which were determined as relative signs between ^{n}J(C–N) and ^{n+1}J(C–N),[8,9] where the absolute signs of which are based on consideration of the lone pair orientation to the spin-coupled carbon.

Thus, in order to obtain further corroborating evidence for the 'absolute signs' of these ^{1}J(N–N) and ^{n}J(C–N) from a different point of view, we tried to relate these relative sign combinations to the sign of ^{1}J(C–H) in the benzene ring. The absolute sign of ^{1}J(C–H) is definitely known to be positive.[15] A strategy tried for this purpose is to relate the sign of ^{1}J(C–H) to that of ^{2}J[C(2),(6)–N(α)], through that of ^{3}J[N(α)–H(2),(6)]. This idea was applied to C(2),(6) of [^{15}N]AAB in CDCl$_3$ and not to those of [^{15}N]acetylAAB in [$^{2}H_6$]dimethyl sulphoxide, because [^{15}N]acetylAAB showed no definite splitting due to ^{3}J[N(α)–H(2),(6)]. Figures 5 and 6 show the results of these trials and the relevant schematic diagrams are shown in Figures 7(a) and (b), respectively. As shown in Figure 5(d), the low- and high-field components, which arise from the one-bond ^{13}C–^{1}H coupling [C(2),(6)L and C(2),(6)H, ^{1}J(C–H) = 160.8 ± 0.3 Hz], appeared mainly as a doublet (5.8 Hz) of doublets (4.3 Hz), although each inner part of the smaller doublet in C(2),(6)L and C(2),(6)H was further split into a doublet (0.8 Hz) owing to second-order couplings with H(2),(6) and H(3),(5) We can easily verify that the larger splitting (5.8 Hz) corresponds to ^{3}J[C(2)–H(6)] or ^{3}J[C(6)–H(2)], with the smaller one (4.3 Hz) to ^{2}J[C(2),(6)–N(α)], since a selective ^{15}N decoupling experiment for N(α) clearly left the larger splitting [Figure 5(c)]. As can be realized from the schematic diagrams for N(α) and C(2),(6), if ^{1}K[C(2),(6)–H(2),(6)] and ^{3}K[N(α)–H(2),(6)] are of the same sign, selective ^{15}N irradiation at a frequency somewhat to high (or low) field from the N(α) chemical shift is expected to cause an effective reduction of the splitting due to ^{2}J[C(2),(6)–N(α)] for C(2), (6)H [or C(2),(6)L]. Furthermore, if the sign of ^{3}J[C(2)–H(6)] {^{3}J[C(6)–H(2)]} is positive, the high doublet in C(2),(6)H would coalesce more effectively than the low doublet. Experimental results in Figures 5(b) and (a), where the irradiation frequencies are shifted by 4 Hz to high and low field from the N(α) chemical shift, respectively, show that this is indeed the case. Thus, the sign of ^{3}J[N(α)–H(2),(6)] was proved as negative.

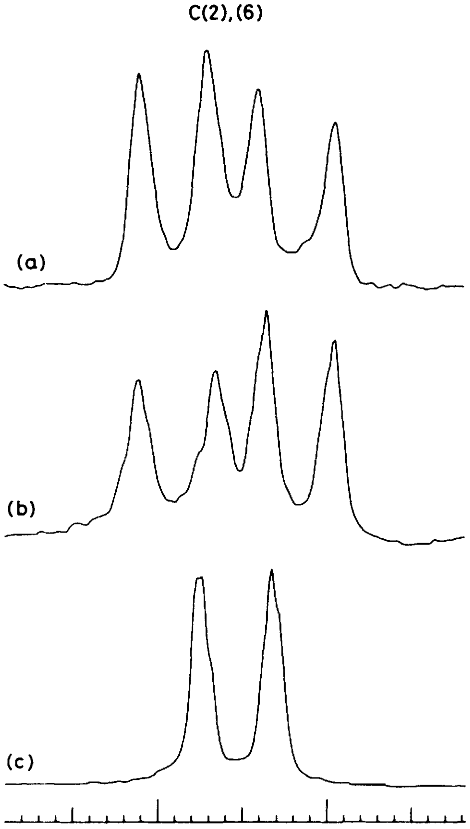

Figure 6. Selectively proton-decoupled ^{13}C n.m.r. spectra of C(2),(6) of [^{15}N]AAB in $CDCl_3$: (a) with selective irradiation at a frequency shifted by 20 Hz from the H(2),(6) chemical shift (7.78 p.p.m.) to lower field; (b) as in (a), but shifted by 20 Hz to higher field; (c) with selective irradiation at the H(2),(6) chemical shift. The ^{1}H irradiation power ($\gamma H_2/2\pi$) was *ca.* 440 Hz. Digital resolution was 0.15 Hz per point. One division is equal to 1 Hz

On the other hand, this negative sign could be correlated to that of ^{2}J[C(2),(6)–N(α)] by selective proton decoupling experiments for C(2),(6). The irradiation power used was such that it can decouple the one-bond ^{1}J[C(2),(6)–H(2),(6)] coupling when it was applied just at the H(2),(6) chemical shift [Figure 6(c)], but leaves the ^{1}J(C–H) as a residual J^{r}(C–H) splitting of 7—8 Hz when applied 20 Hz off-resonance from the H(2),(6) chemical shift [Figures 6(b) and (a)]. As shown in Figure 6(b), when the ^{1}H irradiation frequency was shifted to high field, the J^{r}(C–H) splitting was smaller for the high-field component of C(2),(6), which arises from ^{2}J[C(2),(6)–N(α)], than for the low-field one. The reverse situation was noted in Figure 6(a). These observations clearly indicate that ^{3}K[N(α)–H(2),(6)] and ^{2}K[C(2),(6)–N(α)] are of the same sign [see Figure 7(b)]. Thus, the sign of ^{2}J[C(2),(6)–N(α)] is negative. This agrees with the sign deduced from those of two-bond C(1)–N(β) and C(1′)–N(α) couplings and hence confirms all the absolute signs shown in Table 1. In conclusion, the sign of ^{1}J(N–N) of *trans*-diazenes is negative against our expectation based on the theoretical calculations.[3–6]

Discussion

This embarrassing discrepancy of sign between the experimental results and the theoretical prediction can be settled by considering the signs of ^{1}J(N–N) of hydrazine[3,4] and

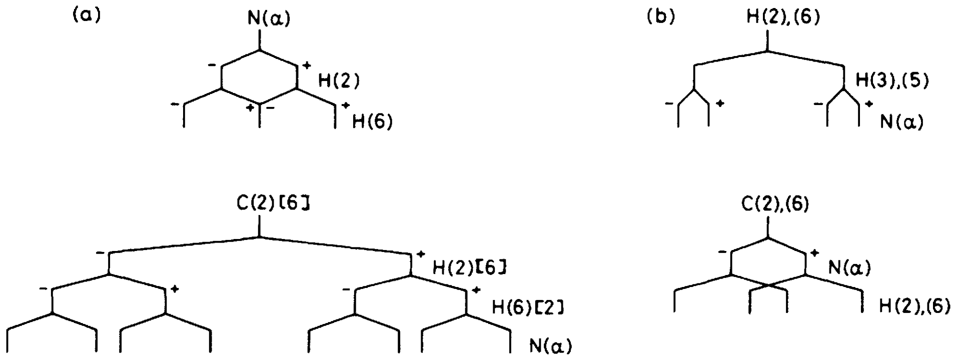

Figure 7. (a) Schematic diagrams for N(α) and C(2),(6) at a proton-coupled state. (b) Schematic diagrams for H(2),(6) and C(2),(6). In C(2),(6), residual J^{r}(C–H) splittings of ^{1}J[C(2),(6)–H(2),(6)] are shown; the other couplings, *e.g.* ^{2}J[C(2)–H(3)], ^{3}J[C(2)–H(6)], and ^{4}J[C(2)–H(5)], are not shown here, because they are fully decoupled at the irradiation power used. ^{1}J[C(2),(6)–H(2),(6)] = 160.8 ± 0.3 Hz, ^{3}J[C(2)–H(6)] {^{3}J[C(6)–H(2)]} = 5.8 ± 0.3 Hz, ^{2}J[C(2),(6)–N(α)] = 4.3 ± 0.3 Hz, ^{3}J[N(α)–H(2),(6)] = 1.5 ± 0.2 Hz, ^{3}J[H(2)–H(3)] {^{3}J[H(5)–H(6)]} = 8.8 ± 0.2 Hz, and J^{r}(C–H) = 7—8 Hz

diazenes[5,6] independently, and also by scaling the integral parameters, $S_N^2(0)$ and $\langle r^{-3}\rangle_N$, employed in the calculations for diazenes. The $S_N^2(0)$ is the density of the valence shell *s* electron at the nitrogen nucleus and $\langle r^{-3}\rangle_N$ the expectation value of the inverse cube of the radius of the valence shell *p* orbitals; the former specifies the magnitude of the Fermi contact (FC) term and the latter those of the orbital–dipole (OB) and spin–dipolar (SD) terms.[16] In the previously calculated values, we notice that only the FC term is dominant in hydrazine,[3,4] whereas the OB term is also important in diazenes.[5,6] Previously reported values (in Hz) are (J^{FC},J^{OB},J^{SD}, total) = (25.6, −11.7, 5.7, 19.6) in *trans*-4-aminoazobenzene[6] and (J^{FC},J^{OB},J^{SD},total) = (−17.9, −4.0, 0.7, −21.2) in 3-methylpyridazine.[5] These were calculated by using one-centre integrals obtained from Slater-type atomic orbitals [$S_N^2(0) = 5.246$, $\langle r^{-3}\rangle_N = 2.472$].[17] Since the sign of the OB term in *trans*-4-aminoazobenzene is opposite to that of the FC term, *i.e.* negative, we can change the sign of ^1J(N–N) of *trans*-4-aminoazobenzene arbitrarily by scaling the relative magnitudes between $S_N^2(0)$ and $\langle r^{-3}\rangle_N$. One-centre integrals thus adjusted to reproduce the observed ^1J(N–N) values of both *trans*-4-aminoazobenzene (−15.5 Hz) and 3-methylpyridazine (−22.1 Hz) were $S_N^2(0) = 3.405$ and $\langle r^{-3}\rangle_N = 5.191$, and the resulting calculated values for ^1J(N–N) of *trans*-4-aminoazobenzene and 3-methylpyridazine were (J^{FC},J^{OB},J^{SD},total) = (10.8, −51.5, 25.2, −15.5) and (J^{FC},J^{OB}, J^{SD}, total) = (−7.5, −17.5, 2.9, −22.1), respectively. Although there remains a question as to the physical meaning of the parameters scaled to such a large extent,[17,18] the need of large modifications from the originally transferred atomic values has also been claimed by Schulman *et al.*[7] and Webb *et al.*[19] for adjusting calculated values to the observed ^{13}C–^{15}N spin-coupling constants of triply bonded nitriles and isocyanides. Thus, it seems reasonable to scale the parameters for the case of an N=N double bond in diazenes, at least in a framework of the self-consistent perturbation theory at the INDO MO level of approximation.[16] It should be noted, however, that the ^1J(N–N) value calculated with the unscaled values of the integral parameters could also give very good fit with that observed in 3-methylpyridazine. Thus, to discuss the validity of scaling the integral parameters, we should await more sophisticated calculations that can accurately evaluate the relative importance of the FC, OB, and SD terms in diazenes.

In conclusion, we think that the sign of ^1J(N–N) of hydrazine in an *anti*-conformation with respect to the two lone pairs is positive as indicated by the theory, if we could determine the sign experimentally. On the other hand, the sign of ^1J(N–N) of *trans*-diazenes is negative as evidenced in the present experiment. This sign reversal is attributable to the large negative contribution from the orbital-dipole mechanism in ^1J(N–N) coupling of an N=N double bond, which is negligible for the corresponding spin–coupling for an N–N single bond of hydrazine.

Acknowledgements

We thank Professor M. Okamoto, Kyoto Pharmaceutical University, for providing facilities to synthesize the materials.

References

1 T. Axenrod, in 'Nitrogen NMR,' eds. M. Witanowski and G. A. Webb, Plenum Press, London, 1973, chap. 5; M. Witanowski, L. Stefaniak, and G. A. Webb, *Annu. Rep. NMR Spectrosc. (London)*, 1977, **7**, 117; R. E. Wasylishen, *ibid.*, p. 245; M. Witanowski, L. Stefaniak, and G. A. Webb, *ibid.*, 1981, **11B**, 12, 110.

2 G. C. Levy and R. L. Lichter, 'Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy,' Wiley-Interscience, New York, 1979, chap. 4.

3 J. M. Schulman, J. Ruggio, and T. J. Venanzi, *J. Am. Chem. Soc.*, 1977, **99**, 2045.

4 J. M. Schulman and W. S. Lee, *J. Magn. Reson.*, 1982, **50**, 142.

5 Y. Kuroda, Y. Fujiwara, and K. Matsushita, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1533.

6 Y. Kuroda, H. Lee, and A. Kuwae, *J. Phys. Chem.*, 1980, **84**, 3417.

7 J. M. Schulman and T. Venanzi, *J. Am. Chem. Soc.*, 1976, **98**, 4701.

8 Y. Kuroda and Y. Fujiwara, *J. Phys. Chem.*, 1981, **85**, 2655.

9 Y. Kuroda and Y. Fujiwara, *J. Phys. Chem.*, 1982, **86**, 4913.

10 R. Lovrien and J. C. B. Waddington, *J. Am. Chem. Soc.*, 1964, **86**, 2315.

11 A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longman, Green, London, 1956, 3rd edn., pp. 626—627.

12 Y. Kuroda, Y. Fujiwara, and K. Matsushita, *J. Magn. Reson.*, 1985, **61**, 149.

13 J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

14 P. E. Hansen, O. K. Poulsen, and A. Berg, *Org. Magn. Reson.*, 1979, **12**, 43.

15 A. D. Buckingham and K. A. McLauchlan, *Proc. Chem. Soc.*, 1963, 144.

16 A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, 1971, **55**, 950; 1973, **58**, 4714.

17 A. D. C. Towl and K. Schaumburg, *Mol. Phys.*, 1971, **22**, 49.

18 J. Kowalewski, *Annu. Rep. NMR Spectrosc.*, 1982, **12**, 81.

19 Tun Khin and G. A. Webb, *Org. Magn. Reson.*, 1978, **11**, 487.

Received 29th April 1985; *Paper* 5/704