Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Spin-coupling Between Directly Bonded ^{15}N-Nuclei

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Summary ^{15}N–^{15}N Coupling constants were obtained for several doubly labelled compounds including cyclic and acyclic nitroamines, which show a correlation with the hybridization of the nitrogen atoms and the conformation of the nitroamine group.

ALTHOUGH ^{15}N n.m.r. spectroscopy is potentially of great use, the low natural abundance (0·36%) and unfavourable sensitivity of the ^{15}N nucleus have limited its applications, but the advent of pulse Fourier transform (FT) spectroscopy has led recently to increased interest in this field.[1–3] Apart from the one-bond ^{15}N–^{13}C coupling constants reported by Binsch and his co-workers[4] only isolated reports of coupling between ^{15}N and other nuclei have appeared.[5] Except for *trans*-azoxybenzene[4] and the recently reported *p*-hydroxyazobenzene,[6] coupling between directly bonded ^{15}N nuclei is unknown and the structural features that influence this coupling have not been systematically investigated. Previous work on ^{15}N–H[3] and ^{13}C–^{13}C couplings[3,7] suggests that study of ^{15}N–^{15}N couplings would provide detailed information about the N–N bond.

Accordingly we have investigated coupling constant data for a variety of N–N bonds in different functional groups and the correlation of these data with molecular structure. We found it necessary to use doubly labelled compounds having a ^{15}N enrichment of 95% at each nitrogen centre.

The ^{15}N–^{15}N coupling constants (Table) are much smaller than those for one-bond ^{15}N–H coupling (60—140 Hz), but this is not unexpected in view of the smaller gyromagnetic ratio of the ^{15}N nucleus. The range of ^{15}N–^{15}N coupling constants ($<$ 20 Hz) is comparable to that for similar couplings between directly bonded ^{15}N and ^{13}C nuclei.[3]

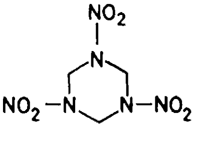
If the principal contribution to the nuclear spin–spin interaction between elements of the first row of the periodic table is considered to arise from the Fermi contact term, the coupling as predicted from theory and MO calculations[8] should be related to the *s*-electron densities at each centre. As a consequence the measured coupling constants can in principle be correlated with the hybridization and/or effective nuclear charge at the nuclei.[8] Although the data are sparse, the Table shows such a trend. *E.g.*, the ^{15}N–^{15}N coupling in *p*-nitrobenzaldehyde phenylhydrazone (10·7 Hz) is significantly greater than that in phenylhydrazine (6·7 Hz), presumably as a result of the incorporation of the terminal amino-nitrogen of phenylhydrazine into the imine bond. Thus the increase in sp^2 hybridization at the latter nitrogen atom parallels the increased coupling. In *trans*-azoxybenzene or *p*-hydroxyazobenzene where both nitrogen atoms may be taken as sp^2 hybridized the coupling increases even further (15 Hz) and finally, in dibenzylnitrosamine, for which there is evidence for substantial N–N *p*–π bonding,[9] the largest coupling (19 Hz) to date has been found. If this interpretation is correct, the ^{15}N–^{15}N coupling in the benzenediazonium ion, where both nitrogens are presumably *sp*-hybridized, should be even greater, although this coupling is not known at present.

TABLE

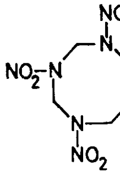
Directly bonded ^{15}N–^{15}N *and* ^{13}C–H *coupling constants*

Compound	$^1J(^{15}N–^{15}N)$/ Hz[b]	Approximate hybridization of N–N bond	$^1J(^{13}C–H)$/ Hz[c]
Phenylhydrazine	6·7[d]	sp^3–sp^3	
p-Nitrobenzaldehyde phenylhydrazone	10·7[d]	sp^3–sp^2	
trans-Azoxybenzene[4]	13·7[e]	sp^2–sp^2	
p-Hydroxyazobenzene[6]	15·0[f]	sp^2–sp^2	
Dibenzylnitrosamine	19·0[d]	sp^2–sp^2	
Dimethylnitramine	4·9[g]		141·5
(II)	8·9[d]		163·4
(III)	4·5[d]		161·7
(IV)	8·5[d]		
(V) [Methyl-(2,4,6-trinitrophenyl)nitramine]	4·9[d]		

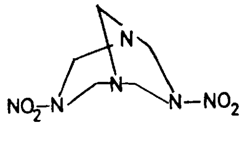
[a] 95% enrichment of ^{15}N at each N atom. [b] ±0·6 Hz. [c] ±0·1 Hz. [d] In Me$_2$SO. [e] In Et$_2$O. [f] In Me$_2$CO. [g] In CDCl$_3$.



(II)

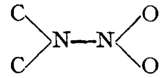


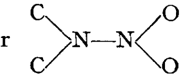
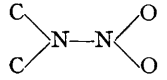
(III)



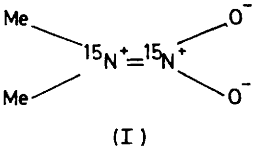
(IV)

The five multiply labelled nitroamines in the Table may be divided into two groups, one in which the ^{15}N–^{15}N couplings are *ca.* 5 Hz and the other *ca.* 9 Hz. The former includes the eight-membered ring compound (III) and the latter the structurally similar six-membered ring compound (II), as well as the bridged tetrazabicyclononane (IV). Although (II) and (III) are structurally similar, they show a significant difference in the ^{15}N–^{15}N coupling, probably arising from the different average conformations that these ring systems can assume.

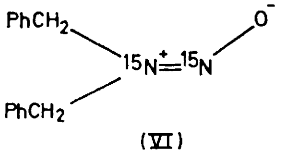
Physical measurements[10] and MO calculations[11] indicate that the molecular geometry of (II) in solution has a higher degree of symmetry than in the crystalline state. In solution the molecule has approximately C_{3v} symmetry with some distortion associated with the nitro-groups. Over a wide range of temperature and in different solvents the n.m.r. spectrum shows the methylene hydrogens[10] and the ring nitrogens to be chemically equivalent. Thus, in solution the molecule is viewed as corresponding to the idealized chair conformation with three planar  groups and the ring undergoes rapid inversion with the cyclic nitrogens oscillating about the planar (sp^2) position.[10]

Although the crystal structure of (III) has been determined,[12] much less is known about its molecular geometry in solution. The presence of only a single resonance in the ^{1}H n.m.r. spectrum[10] indicates that the ring system is undergoing rapid interconversion. However, molecular models reveal that the ring system cannot accommodate four planar  groups without introducing severe transannular nonbonded interactions. In contrast to the situation in (II), this may result in greater average bond-angle distortion or rotation of the NO$_2$ group about the N–N bond, diminishing the π-bonding between the nitrogens. This explanation is consistent with the smaller ^{15}N–^{15}N coupling found in (III). Moreover, in the tetraazabicyclononane (IV) the  groups are constrained into a rigid chair conformation and molecular models indicate little or no impediment to planarity within the latter groups. On this basis, $^1J(^{15}N–^{15}N)$ in this compound might be expected to be comparable to that found in (II), in agreement with the experimental value (8·5 Hz).

It is noteworthy that $^1J(^{15}N–^{15}N)$ for the nitramines listed in the Table is strikingly different from that observed for dibenzylnitrosamine. In dimethylnitramine, for example, the requirement of adjacent positive charges reduces the importance of the polar contributing structure (I) compared with dibenzylnitrosamine (VI). Such a difference would also be consistent with electron diffraction studies which show the N–N bond distance in dimethylnitrosamine (1·41 Å) to be considerably shorter than in dimethylnitramine (1·57 Å).[13]



(I)



(VI)

Finally, although a planar nitramine framework is expected in the acyclic nitramines, dimethylnitramine[14] and methyl-(2,4,6-trinitrophenyl)nitramine (V), the ^{15}N–^{15}N coupling constants found in these compounds appear to be inconsistent with the values and interpretations suggested for the cyclic nitramines. However, in view of the differences in the gross structures and in the one-bond ^{13}C–H coupling constants, it is doubtful whether a comparison of $^{1}J(^{15}N–^{15}N)$ in cyclic and acyclic nitramines is warranted.

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