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A C-13 AND N-15 NMR STUDY OF THE SYN-ANTI-ISOMERISM OF DIAZOCYANIDES

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A ^{13}C and ^{15}N nmr study seriously questions conventional explanations for syn-anti-isomerism of the named compounds, and suggests an alternative modelled after singly bend and doubly bend diazo complexes with transition metal ions.

The reaction of diazonium salts with nucleophiles such as cyanide, hydroxide and bisulfite ions results in the production of meta-stable intermediates known as syn-diazocyanides, syn-diazotates and syn-diazosulfonates, respectively. These compounds isomerize under a variety of conditions to more stable compounds with the designation of anti-isomers. Hantzsch(1) earlier suggested that these transformations were a geometrical case of cis- (syn-) isomers being converted to more stable trans- (anti-) isomers. The only definitive study that supports this postulate was that of Le Fevre(2) who measured the dipole moments of a series of diazocyanides and found them to be consistent with Hantzsch's hypothesis. Later Hodgson and Marsden(3) suggested that the isomerism was of structural type, that is, between isocyanide and cyanide structures. The geometrical isomerism explanation was never satisfactory for the marked differences in the diazo coupling behaviour of these series of compounds with phenols. Here we present some ^{13}C and ^{15}N nmr evidence which suggests an alternate explanation to those given in the past(4).

The ^{13}C and ^{15}N chemical shifts of four substituted diazo cyanides (see formula) are listed in Table 1 together with those for cis- and trans-azobenzenes(5). The $^{13}C(1)$ and $^{13}C(4)$ chemical shifts of the syn- and anti-diazocyanides are similar to those of cis- and trans-azobenzenes, respectively. Most of the carbon nuclei of syn-isomers were found to be more shielded than those of anti-isomers. It was especially true for the chemical shifts of cyano carbons in the compounds studied. This has generally been observed among ^{13}C chemical shfts of cis- and trans-alkene compounds.

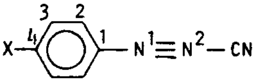

Table 1 ^{13}C and ^{15}N Chemical Shifts of Isomers of Some Benzenediazocyanides and Azobenzene

Nuclei		*p*-CH$_3$O	*p*-Cl	*p*-NO$_2$	*m*-CH$_3$	Azobenzene5)
C(1)	*syn*	151.0	154.4	158.6	156.6	153.3
	anti	149.4	151.8	155.7	153.5	152.5
C(2,6)	*syn*	127.7	130.4	121.7	118.7 123.2	120.5
	anti	127.7	130.6	125.3	122.7 124.3	122.8
C(3,5)	*syn*	114.9	124.0	125.4	140.3 136.3	128.6
	anti	115.5	125.8	125.5	- 138.7	129.0
C(4)	*syn*	166.3	141.9	149.3	129.7	127.3
	anti	167.9	144.4	152.4	129.9	130.9
^{13}CN	*syn*	112.3	110.9	109.5	111.1	-
	anti	116.8	115.7	115.2	115.7	-
N(1)	*syn*	544.4	561.5	569.0	568.0	526.5
	anti	585.1	597.6	604.4	602.7	509.0
N(2)	*syn*	394.0	430.7	454.7	431.0	-
	anti	435.2	463.2	486.1	460.0	-
C^{15}N	*syn*	-	276.6	-	275.9	-
	anti	-	258.8	-	256.5	-

Chemical shifts are in ppm from TMS (^{13}C) and from NH$_3$ (^{15}N).

The internal nitrogens, N(1), in diazocyanides are less shielded than those of corresponding azobenzenes. The same nitrogens, N(1), of the *anti*-isomers are less shielded than those of the *syn*-isomers by an average of 37 ppm. The terminal nitrogen, N(2), of *anti*-isomers are also less shielded than those of *syn*-isomers by 30-40 ppm. This is contrary to the nitrogen chemical shifts of azobenzene5) and a number of diazenes6) where the nitrogens of the *trans*-isomers are always more shielded than those of the *cis*-isomers.

Comparing the carbon-13 chemical shifts values reported for cyano (~110 ppm) and isocyano (~155 ppm) carbons7) and also the nitrogen-15 chemical shifts of cyano (240-260 ppm) and isocyano nitrogens8) (~160-180 ppm) with those observed for the *syn*-isomers, this isomerisation is definitely not of structural nature as suggested by Hodgson and Marsden3).

In Table 2, some ^{13}C-^{15}N and ^{15}N-^{15}N coupling constants are shown for both *syn*- and *anti*-diazocyanides. The nitrogen-nitrogen coupling constants, $J_{^{15}N(1)-^{15}N(2)}$, for *syn*-isomers were found to be larger than those for *anti*-isomers. This is consistent with the results obtained for *cis*- and *trans*-isomers of several diazenes$^{6)}$.

Table 2 Some Coupling Constants of Substituted Benzenediazocyanides (in Hz)

		p-CH$_3$O	*p*-Cl	*p*-NO$_2$	*m*-CH$_3$
N(1)-N(2)	*syn*	23	-	23	-
	anti	15	-	16	-
C(1)-N(1)	*syn*	-	9	8	-
	anti	-	2	3	-
C(1)-N(2)	*syn*	4	4	3	-
	anti	7	7	7	-
N(2)-*CN	*syn*	17	18	19	18
	anti	2	1	2	3

The coupling constants between cyano carbon and terminal nitrogen, $J_{^{15}N(2)-^{13}CN}$, for *syn*-isomers were found to be much larger than those for *anti*-isomers. Many of direct ^{13}C-^{15}N coupling constants for compounds where the lone pairs on nitrogen are well defined and have considerable s characters have been measured and they are all small$^{8)}$. The constants found here for the *anti*-isomers are consistent with these results. The much larger coupling constants found for the *syn*-isomers indicate that the nature of the bonds between cyano carbon and the terminal nitrogen in *syn*-isomers is quite different from those in *anti*-isomers. Closest examples observed are for alkyl diazo compounds (~20 Hz)$^{8)}$. They seem to agree well with the prediction that the Fermi contact term is dominant and that the bonds N-N-CN are linear. This finding suggests strongly that the structure of the *syn*-isomer is not of the *cis*-arrangement but that the N-N-CN bond is linear analogous to those found in complexes of diazonium salts with some transition metal ions$^{9)}$, although the shieldings of the ^{13}C nuclei in *syn*-isomers remain unexplained. The lone pair on the terminal nitrogen is not as well defined as in *anti*-isomers with sp^2 hybridization. From the chemical shifts of the cyano carbon (110-115 ppm), and those of both internal and terminal nitrogens, it is quite evident that the bond N(2)-CN is not ionic. In diazonium salts which have ionic bonds, the chemical shifts are much more shielded (228-247 ppm for N(1) and 314-345 ppm for N(2)$^{10)}$). The more well defined lone pair of the *anti*-isomers indicated above is also consistent with the decreased shieldings of these isomers.

Syn- and anti-diazocyanides including ^{15}N labeled compounds were prepared according to methods described by Le Fevre2) or references cited therein. Carbon-13 and nitrogen-15 nmr spectra were measured on a Bruker WP-80 nmr spectrometer operating at 20.1 MHz and on a Bruker WH-200 nmr spectrometer oprating at 20.28 MHz, respectively. Samples were dissolved in deuterated chloroform. Most of the nitrogen-15 measurements were made on ^{15}N labeled compounds.

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