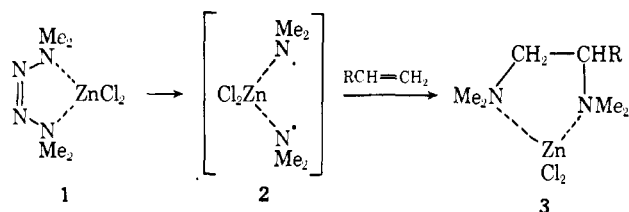
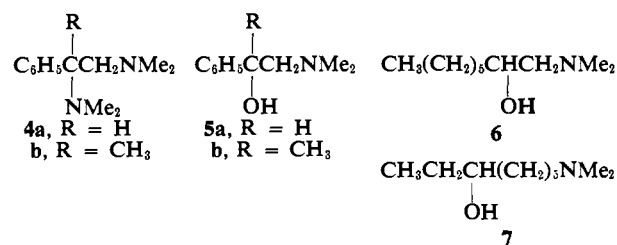


Noltes and van den Hurk<sup>5</sup> prepared a complex of tetramethyl-2-tetrazene (TMT) and zinc chloride whose elemental analysis was consistent with the empirical formula  $C_4H_{12}N_4ZnCl_2$ . On heating between 40 and 60° the complex lost nitrogen. Although no structural data were given for the complex, the authors assumed that it had the structure shown in 1.<sup>6</sup> It seemed likely to us that the loss of nitrogen could yield the biradical species 2. It also seemed likely that 2 could be intercepted by a suitable olefin to give a 1,2-tetramethyl-diamine complex 3.



The complex was conveniently prepared in anhydrous THF<sup>7</sup> by mixing anhydrous zinc chloride (in slight excess) with TMT. The complex could be isolated from this solution by precipitation with dry pentane, but for the preparative experiments described in this report the complex was not isolated. The excess olefin was added to the solution and the mixture was heated under reflux (65°) for 2 hr. The basic components of the reaction mixture were extracted and then separated by glc. The olefins tested included styrene,  $\alpha$ -methylstyrene, stilbene, 1-octene, *cis*- and *trans*-2-butene, cyclohexene, and 3,3-dimethyl-1-butene.

In the absence of oxygen, styrene and  $\alpha$ -methylstyrene gave 30% yields of the diamino adduct 4, stilbene gave only a trace of the adduct (~5%). In the presence of oxygen ( $O_2$  passed over the stirred reaction mixture) both styrene and  $\alpha$ -methylstyrene gave 30–35% of the amino alcohol 5 and 1-octene gave 10–15% of the amino alcohol 6.<sup>8,9</sup> The other alkenes mentioned



failed to give detectable adducts under the conditions employed. The formation of the amino alcohols can be rationalized by initial formation of a hydroperoxide which is then reduced by one of the easily oxidizable

(5) J. G. Noltes and J. W. G. van den Hurk, *J. Organometal. Chem.*, **1**, 377 (1964).

(6) An alternative structure for the complex could be a ten-membered ring dimer. Concerted (or near concerted) loss of two nitrogen molecules from the dimer would also give 2 as an intermediate.

(7) We also used acetone and acetonitrile as solvents. There was no qualitative difference in the reactions in those solvents, except that the complex seemed to be less stable.

(8) All the new compounds had correct elemental analyses and the spectral data (infrared, nmr, and mass spectrometry) were consistent with the assigned structures.

(9) In some runs with 1-octene an important trace (<1%) product was detected. It was *N,N*-dimethyl-6-hydroxy-1-octylamine (7). This product was probably formed by an intramolecular hydrogen atom transfer in the initial 1-(*N,N*-dimethylamino)-2-octyl radical, followed by the capture of the rearranged radical by oxygen. This product is important because it is difficult to rationalize its formation by anything but a radical mechanism.

substances present in the reaction mixture. Two likely reducing agents are unreacted TMT and tetramethylhydrazine, which is a product of the decomposition of the original complex.

These data strongly suggest that the intermediate biradical 2 is involved in the reaction and that selected olefins can be used to trap it. The addition of 2 is not concerted as is indicated by the formation of amino alcohols in presence of oxygen.<sup>10</sup> The reaction is very sensitive to steric effects, as is indicated by the lack of addition to internal olefins and to the highly hindered, terminal olefin 3,3-dimethyl-1-butene.

The biradical 2 is a unique species. It is a biradical formed from two monoradicals by virtue of complexation to a metallic center. At the present time we have no data to indicate whether 2 is predominantly a triplet or a singlet. The addition reaction seems to be radical in nature, but this fact does not prove the triplet multiplicity of the intermediate.

Experiments on the structure of the tetrazene-metal ion complexes, the structures of the intermediates, the reactivity of the complexes as a function of the metal, the tetrazene, and the substrate are under active investigation.

(10) It may be argued that the addition of two dimethylamino groups to styrene may not, in fact, be *via* a diradical or even a radical mechanism. A stepwise process involving initial addition of one amino radical to styrene followed by a capture of a second amino radical seems unlikely to us. In a previous study of additions of amino radicals to styrene and  $\alpha$ -methylstyrene (D. H. Campbell and C. J. Michejda, unpublished), we obtained small yields of monoaddition products (maximum yield 10%) and no diadducts. The fact that the apparent amino radical addition occurs in presence of oxygen simply indicates that oxygen is a poor scavenger of amino radicals. We have observed that fact before, as have others.<sup>11</sup> On the other hand, Roberts and Ingold<sup>12</sup> reported that the highly hindered 2,2,6,6-tetramethylpiperidyl radical was rapidly scavenged by oxygen to give the corresponding nitroxide.

(11) P. W. Jones and H. D. Gesser, *Chem. Ind. (London)*, 566 (1970); *J. Chem. Soc. B*, 1873 (1971).

(12) J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3228 (1973).

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## Geometrical Dependences of Carbon-Nitrogen Coupling Constants. Oximes<sup>1</sup>

Sir:

We report here (Table I) the first systematic demonstration that  $^{13}C$ - $^{15}N$  coupling constants are related to nitrogen lone-pair orientation in structurally rigid molecules and that this property can markedly influence values of *one-bond* coupling constants. Isolated examples of the latter phenomenon have been reported for phosphorus<sup>2</sup> and nitrogen,<sup>3</sup> analogous results are well documented for  $J_{NH}$ .<sup>4,5</sup> Readily available oxime iso-

(1) Presented in part at the 14th Annual Experimental NMR Conference, Boulder, Colo., April 1973.

(2) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3470 (1972).

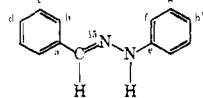
(3) (a) W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, *J. Amer. Chem. Soc.*, **94**, 8501 (1972); (b) However, see H. C. Yeh, H. Ziffer, D. M. Jerina, and D. R. Boyd, *ibid.*, **95**, 2741 (1973).

(4) J. P. Kintzinger and J. M. Lehn, *Chem. Commun.*, 680 (1967).

(5) For reviews, see (a) R. L. Lichter, "Determination of Organic Structures by Physical Methods," Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971, Chapter 4; (b) T. A. Axenrod, "Nitrogen NMR Spectroscopy," G. Webb and M. Witanowski, Ed., Plenum Press, New York, N. Y., 1973, p 261.

Table I. Carbon-13-Nitrogen-15 Coupling Constants in Oximes

Oxime	Solvent	$\delta_C^a$ , ppm	$^1J_{CN}$ , Hz	$^2J_{CN}$ , <sup>b</sup> Hz	$^3J_{CN}$ , <sup>b</sup> Hz	$^5J_{CN}$ , <sup>b</sup> Hz
Formaldehyde	H <sub>2</sub> O	141.6	2.96			
Acetaldehyde ( <i>E</i> )	H <sub>2</sub> O	152.0	4.0	9.0		
Acetaldehyde ( <i>Z</i> )	H <sub>2</sub> O	151.3	2.3	1.8		
Propionaldehyde ( <i>E</i> )	H <sub>2</sub> O	157.1	2.4	7.3	0	
Propionaldehyde ( <i>Z</i> )	H <sub>2</sub> O	157.0	1.6	1.4	0	
2-Butanone ( <i>E</i> )	CDCl <sub>3</sub>	159.2	3.6	0(CH <sub>3</sub> ) 10.5(CH <sub>2</sub> )	0	
2-Butanone ( <i>Z</i> )	CDCl <sub>3</sub>	158.7	3.4	11.1(CH <sub>3</sub> ) 1.8(CH <sub>2</sub> )	0	
3-Pentanone	CDCl <sub>3</sub>	163.6	2.7	10.2(anti) <sup>e</sup> 2(syn) <sup>e</sup>	2.1(anti) <sup>e</sup> 0(syn) <sup>e</sup>	
3-Buten-2-one ( <i>E</i> )	C <sub>6</sub> D <sub>6</sub>	156.9	4.3	1.8(CH <sub>3</sub> ) 11.6(=CH)	6.1	
3-Buten-2-one ( <i>Z</i> )	C <sub>6</sub> D <sub>6</sub>	153.4	3.5	11.6(CH <sub>3</sub> ) 1.8(=CH)	2.4	
Benzaldehyde ( <i>E</i> )	CDCl <sub>3</sub>	150.6	4.8	7.3	2.8	0.8
2-Cyclohexenone ( <i>E</i> )	C <sub>6</sub> D <sub>6</sub>	156.4	5.0	11.0(=CH) 1.4(CH <sub>2</sub> )	6.1(=CH)	
2-Cyclohexenone ( <i>Z</i> )	C <sub>6</sub> D <sub>6</sub>	153.3	4.0	1.8(=CH) 2.4(CH <sub>2</sub> )	3.1(=CH)	
<i>trans</i> -Cinnamaldehyde ( <i>E</i> )	C <sub>6</sub> D <sub>6</sub>	152.6	5.2	9.1	5.6	
<i>trans</i> -Cinnamaldehyde ( <i>Z</i> )	C <sub>6</sub> D <sub>6</sub>	149.6	<i>d</i>	<i>d</i>	3.9	
	CDCl <sub>3</sub>	137.2	7.2	7.9(C <sub>a</sub> ) 5.2(C <sub>e</sub> )	3.4(C <sub>b</sub> ) 2.8(C <sub>f</sub> )	1.0(C <sub>d</sub> )



<sup>a</sup> Oxime carbons only, measured with respect to internal dioxane (in aqueous solution) or solvent carbon resonances and converted to TMS scale [ref 9b, Chapter 2]. <sup>b</sup> Error =  $\pm 0.2$  Hz. <sup>c</sup> With respect to OH. <sup>d</sup> Peaks not observed in enriched compound. <sup>e</sup> Prepared by base-catalyzed decomposition of 1-benzyl-1-phenyl-2-benzenesulfonylhydrazide-2-<sup>15</sup>N: R. L. Lichter, Ph.D. Dissertation, University of Wisconsin, 1967.

mers<sup>6</sup> enriched to 95% with <sup>15</sup>N were chosen for this preliminary study;<sup>7</sup> assignments of carbon resonances rest on off-resonance coherent proton decoupling experiments, comparisons of relative intensities, and reported literature values.<sup>9,10</sup>

In geometrically isomeric oximes, substantial differences in <sup>1</sup>J<sub>CN</sub> arise only when one substituent is a proton; alkenyl substitution induces only small differences, and alkyl none. Within an isomer pair, larger values of <sup>1</sup>J<sub>CN</sub> are associated with those carbons whose resonances lie at lower applied field, e.g., the *E*-aldoxime isomers, in which the two nonhydrogen substituents are anti to each other. These display smaller values of <sup>2</sup>J<sub>NH</sub><sup>4,5</sup> and accord with the difference in <sup>1</sup>J<sub>CN</sub> of pyridine<sup>11</sup> and quinoline<sup>12</sup> compared to benzaldehyde,<sup>13</sup> whose corresponding two-bond nitro-

gen-proton coupling constants are consistent with the above geometrical restrictions. The fairly narrow range of values appears to be enhanced by increasing conjugation in geometrically analogous compounds. This is particularly striking when <sup>1</sup>J<sub>CN</sub> in benzaldoxime is compared with that of mesitaldoxime (2.8 Hz);<sup>14</sup> the trisubstituted ring is expected to be twisted out of coplanarity with the C=N bond.

The geometrical variation of <sup>2</sup>J<sub>CN</sub> also underscores the relationship to nitrogen lone-pair orbital orientation. If pyridine<sup>11</sup> and quinoline<sup>12</sup> are also included, the substituent at nitrogen or carbon appears to have little effect (cf. benzaldehyde oxime and <sup>2</sup>J<sub>N<sub>a</sub></sub> of benzaldehyde phenylhydrazone). Subtler conformational contributions may be evidenced by the difference in <sup>2</sup>J<sub>CN</sub> of the saturated carbons in the 2-cyclohexenone oximes compared with 2-butanone and 3-pentanone oximes; the decrease of <sup>2</sup>J<sub>CN</sub> from benzaldoxime to mesitaldoxime (6.2 Hz)<sup>14</sup> is consistent with diminished conjugation in the latter. Conjugation also appears to affect values of <sup>3</sup>J<sub>CN</sub>, which are easily measurable only in unsaturated systems. The same relation to lone-pair orientation is displayed, although a separate dihedral angle dependence would be difficult to distinguish. Five-bond couplings in benzaldoxime and benzaldehyde phenylhydrazone are comparable to that (0.8 Hz) in benzonitrile oxide, the only other reported five-bond value.<sup>14</sup>

Relative values of <sup>2</sup>J<sub>CN</sub> and <sup>3</sup>J<sub>CN</sub> of unsaturated carbons show a highly definitive dependence on lone-pair orientation; <sup>2</sup>J<sub>CN</sub> is larger in magnitude than <sup>3</sup>J<sub>CN</sub> in the *E* isomers of methyl vinyl ketoxime (1) and

(6) C. G. McCarty, "The Chemistry of the Carbon-nitrogen Double Bond," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 9.

(7) Spectra were obtained largely on a Varian XL-100 spectrometer operating at 25.15 MHz, with noise-modulated complete proton decoupling, and modified<sup>5</sup> for pulsed Fourier-transform operation. A few spectra were determined similarly on a JEOL PS/PFT-100 spectrometer. Enriched hydroxylamine hydrochloride was obtained from Thompson-Packard, Inc.

(8) H. Sternlicht and D. M. Zuckerman, *Rev. Sci. Instrum.*, **43**, 525 (1972).

(9) (a) G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, **94**, 4897 (1972); (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, p 129; (c) Z. W. Wolowski, E. Vauthier, B. Gonbeau, H. Sauvaitre, and J. A. Musso, *Tetrahedron Lett.*, 565 (1972).

(10) A complete discussion of the assignments will be presented in the full paper.

(11) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 5218 (1971).

(12) P. S. Pregosin, E. W. Randall, and A. I. White, *J. Chem. Soc., Perkin Trans. 2*, 1 (1972).

(13) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964).

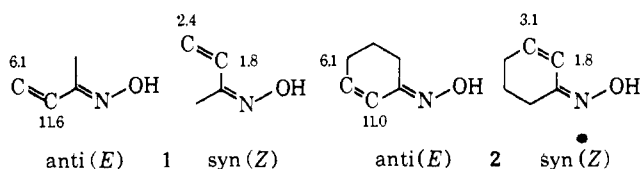
(14) M. Christl, J. P. Warren, B. L. Hawkins, and J. D. Roberts, *J. Amer. Chem. Soc.*, **95**, 4392 (1973).

Table II. INDO MO Calculations of  $J_{CN}$ 

Oxime	$^1J_{CN}$		$^2J_{CN}$		$^3J_{CN}$	
	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
Acetaldehyde ( <i>Z</i> ) <sup>a</sup>	2.3	1.80	1.8	1.76		
Acetaldehyde ( <i>E</i> ) <sup>a</sup>	4.0	1.57	9.0	-3.11		
Pyridine <sup>a,b</sup>	0.4	-1.54	2.4	6.03	3.6	-6.60
Pyridinium ion <sup>a,b</sup>	12.0	-27.5	2.1	7.38	5.3	-8.72
Quinoline <sup>c</sup>	1.4	-2.2 (C <sub>2</sub> )	2.7	8.64 (C <sub>3</sub> )	3.5	-10.74 (C <sub>4</sub> )
	0.6	-1.24 (C <sub>9</sub> )	9.3	-2.58 (C <sub>8</sub> )	0	-4.32 (C <sub>5</sub> )
			2.1	6.32 (C <sub>10</sub> )	3.9	-7.36 (C <sub>7</sub> )
Quinolinium ion <sup>c</sup>	15.9	-27.3 (C <sub>2</sub> )	1	7.37 (C <sub>3</sub> )	4.6	-9.35 (C <sub>4</sub> )
	13.8	-20.9 (C <sub>9</sub> )	1	4.42 (C <sub>8</sub> )	0	-4.73 (C <sub>5</sub> )
			1	5.46 (C <sub>10</sub> )	2.7	-5.73 (C <sub>7</sub> )

<sup>a</sup> Based on geometries described in R. Wasylshen and T. Schaefer, *Can. J. Chem.*, **50**, 2989 (1972). <sup>b</sup> Data from ref 11. <sup>c</sup> Data from ref 12.

2-cyclohexenone oxime (**2**) while the reverse order ob-



tains in the *Z* isomers. These are precisely the structural relationships in quinoline<sup>12</sup> between  $^2J_{N_8}$  and  $^3J_{N_7}$  on the one hand, and  $^2J_{N_8}$  and  $^3J_{N_4}$  on the other. Hence it is unlikely that the differences in the quinoline values are ascribable to the apparent differences in dihedral angle; more likely, enhancement of  $^2J_{N_8}$  over  $^2J_{N_3}$ , and their corresponding values in **1** and **2**, are associated with proximity of the lone pair. Whether agreement in values between corresponding isomers of **1** and **2** reflects a conformation in **1** similar to that in **2** remains open.

The range of  $^1J_{CN}$  values in Table I falls well below that expected ( $\sim 13$  Hz) based on the simple dependence on *s* characters of the coupled nuclei (eq 1) proposed by Binsch, *et al.*,<sup>18</sup> predicated on the assumption that the

$$S_N S_C = 80 J_{NC} \quad (1)$$

Fermi contact term is the dominant spin-spin coupling mechanism; however, lack of agreement with eq 1 does not necessarily exclude dominance of this mechanism. The values calculated on this basis (Table II) using finite perturbation theory in the INDO approximation,<sup>15,16</sup> while displaying poor quantitative agreement with experimental values, nonetheless reproduce several trends, although the absence of experimental sign determinations prevents any detailed comparison. The protonation-induced increases of  $^1J_{CN}$  in pyridine and quinoline are apparent, and the larger magnitude of  $^2J_{CN}$  in *E*- compared to *Z*-acetaldoxime accords with the negative sign calculated for the latter value, which suggests that experimentally  $^2J_{CN}$  is negative, at least in the *E* isomer. This is consistent with the demonstration that lone-pair proximity makes a positive contribution to the reduced coupling constant  $^2K (= 4\pi^2 J / h\gamma_N \gamma_C)$  in phosphorus<sup>17</sup> and nitrogen-containing<sup>3a</sup> systems. The same parallelism exists between experimental and cal-

culated values of  $^2J_{CN}$  and  $^3J_{CN}$  in free and protonated pyridine and quinoline, particularly when the sign dependence on lone-pair proximity is considered.

Finally, it should be noted that  $^1J_{CN}$  differences in isomeric pairs may reflect more subtle differences in bond lengths or angles; C-N bond lengths in aromatic nitrogen heterocycles are about 0.05 Å longer than in nonconjugated compounds;<sup>18</sup> values of  $^1J_{CN}$  are consistently smaller in the former class than in geometrically analogous members of the latter. Indeed, preliminary calculations show that numerical values of the coupling constants are very sensitive to changes in these parameters, although the trends remain unaffected.

Further work is in progress to determine the signs of the couplings and the effect of protonation in order to more definitively assess the theoretical results.

**Acknowledgments.** For support of this work at Hunter College, gratitude is expressed to the City University of New York Faculty Research Award Program, the Research Corporation, and the American Philosophical Society. We are indebted to Dr. V. J. Bartuska of JEOL for his kind hospitality and skillful assistance during determination of some of the spectra. R. W. thanks the National Research Council of Canada for a Postdoctoral Fellowship.

(18) C. Sandorfy, in ref 6, Chapter 1.

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### Fluxional Behavior of (Diene)iron Tricarbonyl Type Complexes

Sir:

During our investigation on the chemistry of tricarbonyl(1,4- $\eta$ -cycloheptatriene)iron and its cycloheptatriene substituted analogs, we were somewhat puzzled to find that the  $^{13}\text{C}$  nmr spectra of the complexes showed only one resonance for the three carbonyl

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