## 1,4-Dimethyl-1,4,5,6-hexahydro-1,2,3,4-tetrazine.

A Cyclic *cis*-2-Tetrazene

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Abstract: The preparation and spectral properties of the title compound (1) are described. The decrease in activation energy for thermal decomposition of 1 compared with the trans model compound tetramethyl-2-tetrazene 2 expected by analogy with azo compounds is not observed; possible reasons are discussed. The oxidation potential of 1 is 570-mV anodic of 2, and the  $a(N_1)/a(N_2)$  ratio for the radical cation is 3, compared with 10 for 2. Both effects are attributed to charge repulsion in the *cis*-tetrazene cation.

ur interest in the thermal decomposition of 2tetrazenes<sup>1</sup> led us to attempt the preparation of the cyclic cis-2-tetrazene, 1,4-dimethyl-1,4,5,6-hexadro-1,2,3,4-tetrazine (1), as the first example of a cis-



tetraalkyl-2-tetrazene. We wished to compare its properties with those of the long-known trans-2-tetrazenes, such as tetramethyltetrazene (2). By analogy with azo compounds, which have  $N_1$  and  $N_4$  replaced by carbon, one would expect 1 to be considerably less stable toward loss of nitrogen than 2. The destabilizing effect of a cis azo linkage compared to a trans one was first noted by Overberger and coworkers,<sup>2</sup> who were unable to isolate the six-ring cyclic analog of azoisobutyronitrile because of its unexpected instability. The destabilization caused by a cis azo linkage appears to decrease the activation energy for thermal loss of nitrogen by some 6-8 kcal/mol. Although trans-2,2'-azoisobutane has  $E_a = 42.8 \text{ kcal/mol},^3$ the five-ring cis analog, 3,3,5,5-tetramethyl-1-pyrazoline, has  $E_a = 36.9^4$  and meso-3,6-dimethyl-3,6-diethylpiperidazene, the closest six-ring analog for which data are reported, 34.3.<sup>5</sup> Steric strain obviously lends additional destabilizaton to acyclic cis azo compounds, but Mill and Stringham<sup>6</sup> have argued that only about 10 of the 20 kcal/mol lowering of  $E_a$  in comparing cisand trans-2,2'-azoisobutane is attributable to steric strain. They suggest that the remainder of the lowering is caused by "electronic repulsive interaction" of the cis lone pairs.

Hoffmann<sup>7</sup> has recently emphasized the importance of

- (5) Thesis of N. A. Porter, Harvard University, 1969. We thank Professor Bartlett for providing this information.
  - (6) T. Mill and R. S. Stringham, Tetrahedron Lett., 1853 (1969).
  - (7) R. Hoffmann, Accounts Chem. Res., 4, 1 (1971).

interactions of lone-pair electrons with  $\sigma$  bonds and the fact that the interaction of an sp<sup>2</sup> lone pair is considerably larger with a trans electron pair than with a cis one. A cis azo compound has the  $N_2$ -C bond in position for a large interaction with the  $N_1$  lone pair, while in a trans azo compound, the lone pairs at  $N_1$ and N<sub>2</sub> are trans and should interact mostly with each other. In agreement with this, calculations of diimide by Robin, Hart, and Kuebler<sup>8</sup> gave 18.5% "H atom character" for the highest lone-pair MO (3b<sub>1</sub>) of the cis form, but only 3.4% for the corresponding MO (4a<sub>g</sub>) of the trans form. This suggests that the destabilizing lone-pair interactions with the  $\sigma$  bonds which must be broken for nitrogen loss to occur are important in causing the experimentally observed lower  $E_{\rm B}$  for cis azo compound decomposition.

On the basis of azo linkage geometry, then, 1 would be expected to be less stable than 2. As previously discussed,<sup>1</sup> we believe that 2-tetrazenes are remarkably stable in comparison with azo compounds, considering the 20-kcal/mol difference in C-N and N-N bond dissociation energies in alkylamines and hydrazines.9 One factor which might be involved would be an increase in  $N_1 - N_2$  bond strength due to interaction as in resonance structure B. Such an effect did not show



up in our studies of 1,4-diaryl-2-tetrazene decompositions,1 but the opposing delocalization of the amino nitrogen lone pair into the aryl ring could have obscured such an effect. Resonance structure B is obviously very important for N-nitroso compounds  $(=N_3 \cdots X \text{ replaced by the more electronegative }=O);$ nitrosodimethylamine was found by nmr to have a 23-kcal/mol activation energy for N-N bond rotation.<sup>10</sup> The importance of B is obviously considerably less for 2 since its methyl group nmr signal remains an un-

<sup>(1) (</sup>a) S. F. Nelsen and D. H. Heath, J. Amer. Chem. Soc., 91, 6452 (1969); (b) S. F. Nelsen, R. T. Landis, L. H. Kiehle, and T. H. Leung, ibid., 94, 1610 (1972).

<sup>(2) (</sup>a) C. C. Overberger, N. R. Byrd, and R. B. Mesrobian, *ibid.*, 78, 1961 (1956); (b) C. G. Overberger, G. Kesslin, and N. R. Byrd, J. Org. Chem., 27, 1568 (1962).
(3) J. B. Levy and B. Copeland, J. Amer. Chem. Soc., 82, 5314 (1960).
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<sup>(8)</sup> M. B. Robin, R. R. Hart, and N. A. Kuebler, J. Amer. Chem.

<sup>(9)</sup> M. D. Room, R. K. Hart, and A. H. Hart, and A. H. Robert, C. Trans. Faraday
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Soc., 57, 23 (1961).
(10) C. E. Looney, W. D. Phillips, and E. L. Reilly, J. Amer. Chem.

Soc., 79, 6136 (1957).

8498

broadened singlet even at  $-70^{\circ.11}$  Although 2 undergoes rapid  $N_1 - N_2$  bond rotation, and the  $N_1$  lone pair is apparently not held in a favorable geometry for resonance interaction with the azo linkage, the steric situation should be rather different for 1, since it should be restricted to half-chair conformations 1a-c. Assuming that the sterically more favorable equatorial



methyl conformations predominate, the amino nitrogen lone pairs should be held in a favorable position for interaction with the  $N_2-N_3$  double bond. This might be expected to stabilize 1 relative to 2 to the extent that double bond character appears in the  $N_1 - N_2$ bond.

Preparation of 1. Our approach to 1 was the obvious one of oxidizing the bishydrazine 5, which was prepared by nitrosation and reduction from symdimethylethylenediamine (3). The cyclization step



proved to be frustratingly difficult and completely unsuccessful using mercuric oxide, lead dioxide, quinone, or potassium perbromate oxidations. In the latter case, we did isolate moderate (17-29%) yields of the solid dimeric 2-tetrazene 6,<sup>12</sup> but no 1 was observed. We finally achieved isolation of 1 in under 5% yields by use of basic oxidation conditions, employing sodium hypochlorite as the oxidant. 1 was characterized by its spectral properties and shown to be monomeric by mass spectroscopy. The uv spectrum of 1 in ethanol shows maxima at 268 nm ( $\epsilon$  5.58  $\times$  10<sup>3</sup>) and 225 (2.97  $\times$  10<sup>3</sup>), quite similar to the uv spectra of *trans*-2-tetrazenes [for 2,  $\lambda_m$  277 ( $\epsilon$  8.98  $\times$ 10<sup>3</sup>) and 250 nm].<sup>13</sup> We had hoped that the  $n \rightarrow \pi^*$ absorption of the cis azo linkage would be discernible, since it occurs at longer wavelength and has a significantly higher  $\epsilon$  in cis azo compounds than in trans ones,<sup>14</sup> but not even a shoulder was observed on the high wave-

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 (13) W. R. McBride and E. M. Bens, *ibid.*, 81, 5546 (1959).
 (14) I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *ibid.*, 91, 1220 (1969).

length side of the intense absorption for either 1 or 2. The n  $\rightarrow \pi^*$  absorption apparently comes at short enough wavelength to be masked by the  $\pi \rightarrow \pi^*$  absorption in cis- as well as trans-2-tetrazenes.

We had hoped to be able to freeze out the N-methylene nmr absorptions of 1 at low temperature and were encouraged by the ease of this for 6, which showed the N-methyl signal at  $\delta$  2.83, and the N-methylene singlet at  $\delta$  3.67 (room temperature) split into an apparent AB quartet at low temperature ( $T_c = +5^\circ$ ;  $\Delta \nu_{AB} =$ 57 Hz,  $J_{AB} = 11.3$ , corresponding to  $\Delta G^{\pm}(5^{\circ})$  of about 13.5 kcal/mol). The high  $\Delta G^{\pm}$  for 6 methylene hydrogen interconversion is our main evidence that 6exists in the trans-trans form shown, for otherwise the flexibility of a 12-membered ring would surely interconvert the methylene hydrogens rapidly on the esr time scale. The nmr spectrum of 1 appeared only as two sharp singlets ( $\delta$  3.12 and 3.04 in 2:3 ratio at room temperature,  $CDCl_3$ ), and although the positions moved slightly as the temperature was lowered, the lines remained sharp to  $-120^{\circ}$  in CH<sub>2</sub>Cl<sub>2</sub>, as low as we could get in temperature. Since ring inversion converts 1a to the mirror image of 1c, if the equilibrium constant between 1c and 1a were large (as expected on steric grounds), only freezing out of nitrogen conversion would be required to freeze out the methylene signal. If, however, 1b were the predominate conformation, ring inversion as well as nitrogen would need to be frozen out to observe freezing out of the methylene signal. The methylene signal of 7,



a nonconjugated bis(azamethyl)cyclohexene, freezes out with a  $T_c$  of  $-120^{\circ}$ .<sup>15a</sup> The methylene signal of 1 is not even broadened at this temperature, which is consistent with flattening of the amino nitrogens of  ${\bf 1}$ by interaction with the N=N bond, but gives no indication of how much flattening may be occurring. The cyclic tetrazene does not need to force adjacent methyl groups past each other during inversion processes, which Jones and coworkers<sup>15b</sup> have argued is the most important single factor in causing detectably slow ring and nitrogen inversions.

Decomposition of 1. The rate of the thermal decomposition of 1 was investigated by gas evolution in tetralin, for comparison with that of 2 (see Table I). Gowenlock and coworkers<sup>16</sup> have studied the vapor-

Table I. Rate of Decomposition of 1 in Tetralin

Temp, °C	$k, \times 10^4$	No. of runs
129.7	$0.96 \pm 0.06^{a}$	2
138.8	$2.66 \pm 0.2^{a}$	3
144.2	$5.21 \pm 0.35^{a,b}$	5
138.8 (compd 2)	0.27	1

<sup>a</sup> Range quoted includes all the observed rate constants. <sup>b</sup> Concentration varied from 0.014 to 0.069 M without affecting the observed rate.

(15) (a) J. E. Anderson, ibid., 91, 6374 (1969); (b) R. A. Y. Jones,

<sup>(11)</sup> W. M. Tolles, D. W. Moore, and W. E. Thun, J. Amer. Chem. Soc., 88, 3476 (1966). We have extended the temperature range to -120° without observing broadening.

A. R. Katritzky, and R. Scaltergood, Chem. Commun., 644 (1971). (16) B. G. Gowenlock, P. P. Jones, and D. R. Snelling, Can. J. Chem., 41, 1911 (1963).



Figure 1. The room temperature esr spectrum of  $1 \cdot +$  in butyronitrile and a simulation using the splittings listed in Table II.

phase decomposition of 2 and discuss the relatively wide variation of their results with those in the literature. In solution less work has been done, but our single determination at 139° in tetralin and that of Erusalimsky and coworkers<sup>17</sup> at 145° in cumene agree reasonably well with vapor-phase studies, which give  $\Delta H^{\ddagger} = 36.1 \text{ kcal/mol}, \Delta S^{\ddagger} = 4.7 \text{ eu}$ . The recent work of Michejda and Hoss,<sup>18</sup> run at 0.2 *M* in benzene, gives an extrapolated rate at 139° about four times the rate we observed in tetralin; we agree with these authors that their activation enthalpy of 45 kcal/mol is suspiciously high.

Although the 15° temperature range studied is not wide enough to make the activation parameters calculated for the decomposition of  $1 (\Delta H^{\pm} = 38 \text{ kcal/mol}, \Delta S^{\pm} = 17 \text{ eu})$  very accurate, it is clear that there is not a 6-8 kcal/mol decrease in  $\Delta H^{\pm}$  between 2 and 1 (as would be expected using azo compounds as models). One possible reason for this could be that the greater conformational restriction of 1 compared to 2 increases the amount of amino lone-pair interaction with the 2,3 bond, as suggested in the introduction. Another is that the azo linkage lone-pair interaction with the N-N bond of 1 might be considerably less important than with the C-N bond of an azo compound.<sup>19</sup>



Figure 2. The esr spectrum of  $1 \cdot +$  in butyronitrile at  $-95^{\circ}$ .

The products from the thermal decomposition of 1 were not investigated fully, but no *sym*-dimethylethylenediamine (3) or formaldehyde *N*-methylimine trimer (10) was observed, and materials of low volatility predominated. In contrast, the only organic product from room temperature photolysis of 1 observed by nmr or vpc was 10, presumably arising by trimerization of the formaldehyde *N*-methylimine (9) expected upon cleavage of a 1,4 diradical formed upon nitrogen evolution (8). The mass spectrum of 1 also showed little but



parent ion and products of three bond cleavage. At 70 eV, the major peaks were m/e 42 (100), 43 (53), and 114 (P, 45); the only other peak over 3% of the intensity of 42 was 71 (P - (15 + 28), 7). Loss of nitrogen from the radical cation must be rapidly followed by C-C cleavage.

The Radical Cation of 1. The redox behavior of 1 and 2 was examined by cyclic voltammetry. In acetonitrile, at a gold electrode, both showed reversible oneelectron oxidation waves,  $E_{1/2} = 0.98$  V (vs. sce) for 1 and 0.41 V for 2. The 570-mV difference in oxidation potential seems most easily explained by the electrostatic effect of forcing a cis geometry for the radical cation of 1, since the highly positively charged N<sub>1</sub> and N<sub>4</sub> nitrogens are constrained to be considerably closer together in  $1 \cdot +$  than  $2 \cdot +$ .

The esr spectrum of  $1 \cdot +$  was easily observed upon electrolytic oxidation of 1 in an esr cell and was quite complex (Figures 1 and 2). We had difficulty in analyzing this spectrum, although it was clear that some splittings must be nearly multiples of others in order to

<sup>(17)</sup> B. L. Erusalimsky, B. A. Dolgoplosk, and A. P. Kavunenko, J. Gen. Chem., USSR, 27, 301 (1957).

<sup>(18)</sup> C. J. Michejda and W. P. Hoss, J. Amer. Chem. Soc., 92, 6298 (1970).

<sup>(19)</sup> For evidence from oxidation potentials that a lone-pair interaction with a perfectly aligned C-C bond is far larger than with a CN bond, see S. F. Nelsen and P. J. Hintz, *ibid.*, 94, 7114 (1972).

give the relatively large alternations in amplitudes observed across the spectrum. Although less resolution was obtained in an esr cell which would fit inside the low-temperature dewar, our best clues for assignments of the better resolved room temperature spectra came from the  $-95^{\circ}$  spectrum in butyronitrile<sup>20</sup> (Figure 2). Although all lines were broad, there is great decrease in intensity between the center and outer regions, an obvious "alternating line width effect."21 Of the four types of spin-bearing nuclei present in  $1 \cdot +$ , only the four methylene hydrogens, which occur in two pairs if the ring is not flat, could show such an effect. The 1:4:6:4:1 quintet caused by these four hydrogens at a rapid interconversion rate would go to a 1:-:4:-:1 three-line pattern at the interconversion rate corresponding to maximum broadening.<sup>21</sup> The separation of the largest lines in the center and outer region of the  $-95^{\circ}$  spectrum was 35.1 G, corresponding to a 17.5-G methylene hydrogen splitting.

To give a rough estimate, a 2.5–3 kcal/mol  $\Delta G^{\pm}$  for "ring and nitrogen" inversion, interconverting the two types of hydrogens, would give the observed alternating line width behavior, assuming  $-95^{\circ}$  corresponded to the temperature of maximum broadening and that the ratio of  $a(H_{ax})$  to  $a(H_{eq})$  was in the range of 2-2.4.<sup>22</sup> Unfortunately, only the average *a* value for the two types of methylene hydrogens is known.

The visible lines in the central portion of the  $-95^{\circ}$ spectra only correspond to two types of nuclei, a 10.5-G multiplet for which five components are easily distinguishable and a narrower 3.17-G five component splitting. No splitting corresponding to the fourth type of nucleus present was apparent. We assign the 10.5-G splitting to the methyl hydrogens and the 3.17-G splitting to the smaller  $(N_2, N_3)$  nitrogen splitting. At these temperatures, anisotropic broadening has become large enough so that the observed peak-to-peak amplitudes for the  $N_2, N_3$  nitrogen splitting deviate significantly from the isotropic 1:2:3:2:1 intensities expected at room temperature. The form for the line width equation<sup>23</sup> under such conditions is  $\Delta H = A(M_n)^2 + BM_n$ + C, where A, B, and C are constants,  $\tilde{M}_n$  is the spectral index number,<sup>23</sup> and  $\Delta H$  is the line width. Although the commonest case is for B to be enough larger than A so that a continuously increasing line width is observed, the structually related 1,2-dimethylaminoethylene cation<sup>24</sup> showed A = 3B, giving a line width which increased with  $|\tilde{M}_n|$ , and we have observed the A term dominating the B term in hydrazine cations.<sup>25</sup> We presume that the larger  $(N_1, N_4)$  nitrogen splitting has such a large A value that only the central component stands out and is readily observed; we have observed this effect in hydrazine cations<sup>25</sup> as well. With a knowledge of the approximate sizes of the splittings, we were able to analyze the room temperature spectrum. The coupling constants used in the simulation shown in Figure 1 are listed in Table II; we believe the splittings to be correct to  $\pm 0.05$  G.

(20) For low-temperature electrolysis in butyronitrile, see R. P. van Duyne and C. N. Reilley, Anal. Chem., 44, 142 (1972).

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- (24) B. C. Gilbert, R. H. Schlossel, and W. M. Gulick, Jr., J. Amer. Chem. Soc., 92, 2974 (1970). (25) S. F. Nelsen, unpublished results.

Table II. Coupling Constants for  $1 \cdot +$  and  $2 \cdot +$  at Room Temperature

Species solvent	1 · <sup>+</sup> PrCN	$2 \cdot a$ Acetone
a(4 H)	12.35	11.72 (6 H)
a(6 H)	10.27	10.45 (6 H)
$a(N_1, N_4)$	9.64	10.93
$a(\mathbf{N}_2,\mathbf{N}_3)$	3.29	1.07
Line width	0.25	

<sup>a</sup> Data of ref 11.

Comparison of the splittings of  $2 \cdot 1^{11}$  with those of  $1 \cdot +$  shows that the greatest difference occurs in  $a(N_2, N_3)$ , which is three times as large in the *cis*- as in the *trans*tetrazene cation. This suggests that forcing the highly positive  $N_1$  and  $N_4$  atoms to lie nearer to each other caused repulsion of the spin toward N<sub>2</sub>, N<sub>3</sub>. As estimated from the methyl splitting, however, the  $\rho(N_1, N_4)$ of  $0.42^{11}$  for  $2 \cdot +$  only decreased to 0.39 for  $1 \cdot + .26$  The large inequivalence of the methylene hydrogen splittings of 1 + at low temperature requires appreciable deviation from planarity at  $N_1$  and  $N_4$  in this radical cation, which presumably means that there is not pure  $sp^2$  hybridization at N<sub>1</sub> and N<sub>4</sub> in the radical cation. Although greater s hybridization in the orbitals at  $N_1, N_4$  of 1 + than of 2 + would be expected to raise $Q(N_1, N_4)$ , we do not believe that our present knowledge of nitrogen splittings allows assignment of spin densities in these systems with the expectation of reasonable accuracy. We suggest that the large difference in  $a(N_2, N_3)$  in ions as similar as  $1 \cdot +$  and  $2 \cdot +$  shows that nonbonded inductive effects are quite large and must be taken into account in spin density calculations.

## **Experimental Section**

N, N'-Dimethyl-N, N'-dinitrosoethylenediamine (4) was prepared in 50-60% yield by the method of Schneider.28 One crystallization from ethanol-ether gave material which melted at  $54-56^{\circ}$ ; several recrystallizations were required to obtain the literature melting point of 60–61  $^\circ$ 

N, N'-Dimethyl-N, N'-diaminoethylenediamine (5) was prepared by the method of Iwamura.<sup>12</sup> About 10% of a solution of 29.2 g (0.2 M) of 4 in 200 ml of THF was added to 15.2 g (0.4 mol) of LiAlH4 in 300 ml of ether, and the solution was stirred mechanically at room temperature until the exothermic reaction began (about 5 min). The flask was cooled, and the remainder of the dinitrosoamine solution was added dropwise. After about half was in, more ether was required to keep the mixture fluid enough to allow stirring. After warming to room temperature overnight, the excess LiAlH<sub>4</sub> was decomposed with 200 ml of 95% alcohol and the mixture was gravity filtered; the filter cake was washed with ethanol and ether, and the filtrate was dried with magnesium sulfate. Vacuum distillation afforded 12.55 g (53%) of the hydrazine 5: bp  $57^{\circ}$  (0.1 mm), which solidified at ice temperature (mp around 25°); nmr  $(C_6D_6) \delta 3.10$  (s), 2.59 (s), 2.39 (s), 2:2:3 integration ratio. The hydroscopic dihydrazine was allowed to react with oxalic acid dihydrate in aqueous ethanol to give the dioxalate, mp 178-179°. Anal. Calcd for C<sub>8</sub>H<sub>18</sub>N<sub>4</sub>O<sub>8</sub>: C, 32.19; H, 6.08; N, 18.78. Found: C, 32.54; H, 6.11; N, 18.64.

1,4-Dimethyl-1,4,5,6-tetrahydro-1,2,3,4-tetrazine (1) was only obtained in about 4% yield from the dropwise addition of 99 ml (0.06 mol) of Clorox to a solution of 3.36 g (0.0285 mol) of 5 in 60 ml of water containing 5-14 g of sodium hydroxide (the amount of base did not affect the yield) at  $-5^\circ$ , stirring 18 hr at  $0^\circ$ , and extract-

<sup>(26)</sup> For 2,3-diaza-2,3-dimethylbicyclic hydrazine cations, 27 a(N) was observed to increase substantially with increasing ring strain, although  $a(CH_3)$  was relatively insensitive. Clearly,  $a(CH_3)$  is not a good way of estimating  $\rho(N)$  in at least the more strained of these systems.

<sup>(27)</sup> S. F. Nelsen and P. J. Hintz, J. Amer. Chem. Soc., 92, 6215 (1970).

<sup>(28)</sup> P. Schneider, Ber., 28, 3072 (1895).

ing with 4  $\times$  20 ml aliquots of methylene chloride. After concentration and tlc on silica P-254 (chloroform), a material containing a yellow impurity ( $\lambda_m$  430) was obtained. Vpc on a 5 ft  $\times$  0.25 in. 15% XF 1150 on 60-80 mesh Chromosorb column at 125–135° removed the impurity, giving 1 as a colorless oil which melts below  $-30^\circ$ . Attempts to prepare the picrate of 1 led to nitrogen evolution: high-resolution mass spectroscopy, obsd mass 114.0905, calcd for C\_4H\_{10}N\_4 114.09054; ir (CCl<sub>4</sub>) 1450 (br), compared to 1480 (br) for 2.

Esr spectroscopy was performed using Varian E15 equipment and Varian electrolysis cells.

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## The Stereochemical Dependence of <sup>15</sup>NCH and <sup>13</sup>CH Coupling Constants in Oxaziridines<sup>1</sup>

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Abstract: The stereochemical dependence of <sup>13</sup>CH and <sup>15</sup>NCH coupling constants has been investigated in a series of diastereomeric (Z)- (cis) and (E)- (trans) oxaziridines. In both cases the reduced coupling constant (K) has been found to be more positive in the Z isomer where the nitrogen lone pair of electrons is cis to the ring proton. The absolute sign of  ${}^{2}K({}^{15}NCH)$  in a representative (Z)-oxaziridine was shown to be positive, while that of  ${}^{1}K({}^{15}N-{}^{13}C)$  was found to be negative, the first demonstrated negative one-bond C–N reduced coupling constant. It is suggested that a cis lone pair of electrons may make a positive contribution to K by direct (*i.e.*, "through space") orbital overlap.

There is considerable evidence that the magnitude of nuclear spin coupling constants can be affected by the presence of proximate lone pairs of electrons. The influence of lone pairs of electrons on indirect coupling between two nuclei may be divided into two types: (I) the lone pair formally situated on either of the coupled atoms, or (II) the lone pair formally situated on a third atom.

Several examples of type I effects that have been recently reported involve PH or NH coupling constants, where the phosphorus or nitrogen atom possesses a lone pair of electrons. Thus, the considerable difference in  ${}^{2}J({}^{15}NCH)$  for the protons  $H_{A}$  and  $H_{B}$  in imines, hydrazones, and oximes (1a and 1b), and in the aziridine 2 has been ascribed to the orientation of the nitrogen lone pair.<sup>3-5</sup> Axenrod, *et al.*,<sup>6</sup> have shown that the magnitude of  ${}^{3}J({}^{15}NNCH)$  in a series of *N*-nitrosamines is markedly dependent on whether the proton is cis or trans to the nitrogen lone pair; additionally,

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(6) T. Axenrod, P. S. Pregosin, and G. W. A. Milne, *Chem. Commun.*, 702 (1968).



 ${}^{2}J({}^{14}NCH)$  and  ${}^{3}J({}^{14}NCCH)$  also appear to be stereochemically dependent in aziridines, imines, and oximes.  ${}^{4b.7,8b}$  The examples of stereospecific  ${}^{15}NH$  coupling measured to date are too numerous to describe and have recently been reviewed quite adequately.<sup>9</sup> Gagnaire, *et al.*,<sup>10</sup> have extensively investigated the

(9) T. Axenrod in "Nitrogen NMR," G. Webb and M. Witanowski, Ed., Plenum Publishing Co., New York, N. Y., in press.

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