state steric destabilizing effect over both the *tert*-butyl (**6a**) and *tert*-heptyl (**6c**) azoalkanes.

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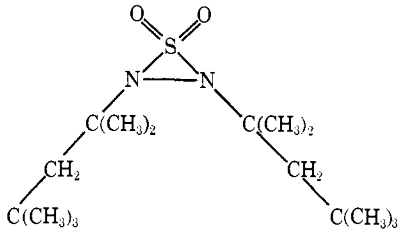
Crystal and Molecular Structure of Bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-Dioxide

Sir:

We wish to report the first detailed structural information on a three-membered ring composed entirely of heteroatoms. Previously, oxadiaziridines[1,2] represented the only ring system made up solely of heteroatoms which had been isolated and characterized. A crystalline sample of a second and more stable three-membered ring system has now been prepared[3] and the structure of a substituted thiadiaziridine dioxide example (**1**) of this system is reported herein.



1

The title compound crystallizes in the orthorhombic space group $Pca2_1$, with cell dimensions: $a = 14.811 \pm 0.001$, $b = 7.951 \pm 0.001$, and $c = 17.059 \pm 0.002$ Å. A complete set of three dimensional X-ray data was taken on a G.E. XRD-490 automated diffractometer system using Cu $K\alpha$ radiation and stationary crystal–stationary counter techniques out to a 2θ limit of 120° ($d = 0.89$ Å). A total of 1012 reflections (58% of the 1754 measured) were considered observed based on our statistical criteria. The data were corrected for $\alpha_1 - \alpha_2$ splitting and absorption, followed by the usual $1/LP$ corrections.

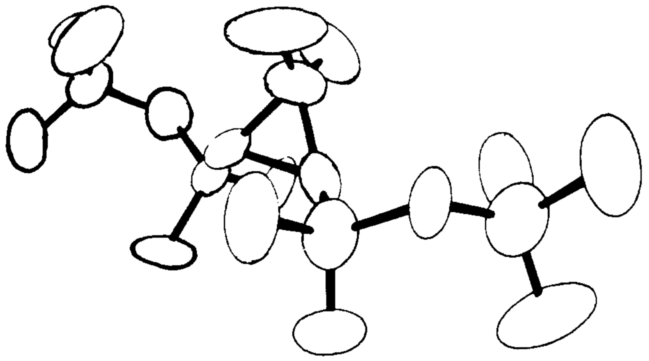


Figure 1. Projective view of bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide.

The S–S vectors were identified on a Patterson map and used to phase the subsequent Fourier map (at a value of $R = 0.52$). Two additional peaks were found and assumed to be the oxygen atoms; the process was repeated ($R = 0.43$), and from that point on alternating least-squares and Fourier techniques resulted in all nonhydrogen atoms being identified ($R = 0.117$ for the final isotropic refinement). Conversion to anisotropic temperature factors followed by further least-squares refinements lowered the value of the reliability index to $R = 0.097$. The results, at this stage, are reported herein and are shown in Figure 1. Further work in locating the 34 hydrogen atoms and the final refinement of the structure are complicated by the relatively large thermal motion already evident in the nonhydrogens and the anticipated rotation of the methyl groups.

The trans configuration of the compound is unambiguously determined and substantiates the previous assumption based on chemical and nmr results. The large thermal motion of the atoms evident thus far obscures any trends in the bond distances of the two octyl side chains. The S–N average bond length of 1.62 Å is shorter than a value of 1.67 Å previously determined[4] for an analogous bond in a noncyclic system. The N–N bond (1.67 Å) is significantly longer than any analogous distance (for example, the 1.48-Å distance for the C–N bond in aziridine itself[5]) and is, in fact, bracketed between the values of 1.64 and 1.71 Å found for the admittedly lengthened[6,7] N–N bond in N_2O_4. Such lengthening may well be the only way that the NSN angle of 62° can be maintained at a value near 60°. For example, if one were to assume a "normal" N–N distance even as long as 1.48 Å and still maintain the present S–N distances, then the resultant NSN angle would be lowered to 52°. However, as a consequence of the ring maintaining this angle at the sulfur, the N–N bond is appreciably weakened. This conclusion suggests that the removal of the magnetic nonequivalence of the two methyl groups closest to the ring nitrogens in the nmr[3] may proceed through a bond breaking, inversion, and bond re-formation mechanism.

Acknowledgment. Partial support of this project by the National Science Foundation (GU-2632) is gratefully acknowledged.

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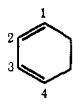
Conformation of Olefin–Iron Carbonyl Complexes from Long-Range Proton Magnetic Resonance Couplings

Sir:

Efforts to define the nature of diene–iron carbonyl complexes based upon pmr data have brought forth

Table I. Experimental Pmr Coupling Constants[a]



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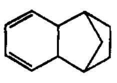

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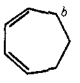

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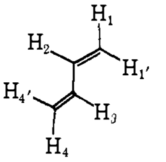

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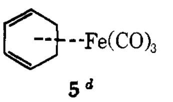
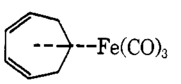


5[d]



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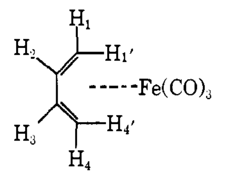
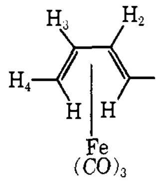


7

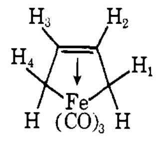
	1	2	3	4	5	6	7
$J_{1,2}$	9.56	9.69	11.55	10.13	6.62	7.69	7.02 (6.9)
$J_{1,3}$	1.02	0.99	0.67	−0.86	1.41	1.20	1.06 (0.7)
$J_{1,4}$	1.08	0.99	0.72	1.27	0.18	0.16	0.05 (0.0)
$J_{2,3}$	4.95	5.47	6.89	10.35	4.21	4.76	4.79 (4.5)
$\Delta\nu_{1,2}$ (Hz)[c]	29.7	20.5	14.5		238.9	201.0	
$J_{1,1'}$				1.70			2.46 (2.5)
$J_{1',2}$				16.90			9.19 (8.2)
$J_{1',3}$				−0.79			−0.78 (0.0)
$J_{1',4}$				0.60			0.11 (0.0)
$J_{1',4'}$				0.71			0.41 (0.0)

[a] *J*'s are in Hz.[5] The relative *J* signs of the Fe complexes were derived by input of + or − signs for the vicinal and long range *J*'s and comparing the spectral plots to the experimental. The relative sign of $J_{1,4}$ in **7** could not be determined but a + sign is preferred based upon calculations within M. Barfield and B. Chakrabarti, *J. Amer. Chem. Soc.*, **91**, 4346 (1969); and M. Bacon and G. E. Maciel *Mol. Phys.*, **21**, 257 (1971). The experimental error is estimated at $\simeq\pm0.1$ Hz. [b] Data from ref 8. Using dicyanoheptafulvene[10] as a model, *J* values expected for a planar conformation are $J_{1,3} = 1.1$, $J_{1,4} = 0.7$, and $J_{2,3} = 8.0$ Hz. [c] **1** and **3** at 300 MHz; **2**, **5–7** at 100 MHz. [d] A. L. Segre. L. Zette, and A. D. Corato, *J. Mol. Spectrosc.*, **32**, 296 (1969).

several contrasting structures, with A and B being the most frequently cited.[1] The latest magnetic resonance data (^{13}C and ^{1}H) reported on these complexes has been interpreted as favoring a structure somewhat intermediate between A and B, which has a significant H_1–H_2 dihedral angle of *ca.* 45°.[2] On the other hand, a three-dimensional X-ray structure determination has supported A, but the positions of the H atoms were not obtainable[3]



A



B

We have examined the ^{1}H spectra of six- and seven-membered ring olefin–$Fe(CO)_3$ complexes, and we have redetermined the pmr parameters for the butadiene complex. Our results are reported below, and they require a description of the relative position of the H_1–H_4 atoms in the complexes which is at variance with the most recent pmr interpretation.[2]

The pmr 60-MHz spectra of iron tricarbonyl complexes of 1,3-cyclohexadiene (**5**), 1,3-cycloheptadiene (**6**), and butadiene (**7**) were published some years ago,[4] and a partial analysis of the pmr spectrum of the latter has been reported.[1e] We obtained spectra of these three complexes at 100 MHz and in each case generated a set of parameters by computer which gave a good fit of the experimental (Table I).[5] In order to provide a basis for interpretation of the *J* values obtained for these complexes, several model cyclic olefins were examined by pmr. Proton coupling constants for 1,3-cyclohexadiene (**1**) were obtained from a 300-MHz spectrum which gave a well-defined AA'BB' multiplet.[6] Similar data are available for 1,3-cycloheptadiene (**3**) from earlier work in our laboratory.[8] The C–C double bonds in each of these dienes are known to be noncoplanar,[8] so we analyzed the spectrum of tricycloundeca-3,5-diene (**2**),[9] which can be assumed to have a planar diene chromophore from inspection of Drieding models. In addition pmr coupling constants are available for a variety of tris unsaturated seven-membered ring compounds which are known to be entirely coplanar.[10]

Dissection of pmr *J*'s into σ and π contributions for systems with olefinic bonds has provided a useful heuristic model.[7,11,12] In this regard two primary considerations will be valuable in comparing the *J* values in Table I: (a) the C=C bonds of an olefin are usually stretched upon complexation, and (b) the π increment to H–H coupling should be perturbed in the diene–$Fe(CO)_3$ complexes.[13] Each of these factors must be in

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(1) (a) M. L. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959); (b) T. A. Manuel, *Inorg. Chem.*, **3**, 510 (1964); (c) H. S. Gutowsky and J. Jonas, *ibid.*, **4**, 430 (1965); (d) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 40 (1964); (e) H. G. Preston, Jr., and J. C. Davis, *J. Amer. Chem. Soc.*, **88**, 1585 (1966); (f) W. R. Roth and J. D. Meier, *Tetrahedron Lett.*, 2053 (1967).

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(13) For a general discussion on iron carbonyl complexes, see F. A. Cotton and G. A. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, Chapter 23.

part responsible for the net decrease in the magnitudes of most of the vinylic couplings observed between the dienes and the diene complexes (Table I).

The J values obtained for the iron complexes do allow meaningful discussion of the relative orientation of the vinyl C and H atoms, but only after several competing coupling mechanisms have been unraveled. It can be assumed that the effect of (a) above will be very large for the three-bond J's and minimal for the four- and five-bond J's.[14] The results of several semiempirical calculations of the relative σ and π contributions to vinylic coupling have been published.[15] There is reasonable agreement among these calculations and in conjunction with experimental data the following relationships have been identified: (i) σ and π contributions to long range J's and σ contributions to vicinal J's are sensitive to H–H orientation;[14,15f] (ii) ${}^3J$ is σ dominant with π coupling estimated to contribute *ca.* 8–14% for cis coupling;[15a,e,g] (iii) there is disagreement regarding the relative σ and π contributions to ${}^4J$;[16] however, the π component of ${}^4J$ appears to be minimal for H–H atoms trans-coplanar ("W" arrangement) and it becomes dominant as coplanarity between H atoms is lost;[12b,15d–f] and (iv) the π contribution to ${}^5J$ is also sensitive to relative H–H orientation. In a cisoid diene ${}^5J$ is predominantly π in character, as opposed to the trans–trans ${}^5J$ in a transoid diene which has nearly equivalent π and σ character.[12b,15d–f] Information of the relative signs of the σ and π vinylic couplings is also important; both theory and experiment indicate that for a cisoid diene ${}^2J_\sigma$, ${}^3J_\sigma$, ${}^3J_\pi$, and ${}^5J_\pi$ are plus in sign while ${}^2J_\pi$, ${}^4J_\pi$ are minus and both ${}^4J_\sigma$ and ${}^5J_\sigma$ may vary in sign as a function of H–H orientation.

Attachment of $Fe(CO)_3$ to dienes **1**, **3**, and **4** results in a decrease in magnitude of the vicinal J's by ~30–40% (${}^3J$'s of **1** and **3** adjusted to reflect a planar conformation). The X-ray of **7** shows a stretching of the sp^2–sp^2 double bond for **4** → **7** of *ca.* 0.11 Å,[13] which according to Karplus would decrease $J_{1,2}$ by ~32%.[14] Assuming for complexes **5**–**7** that the π contribution to $J_{1,2}$ approaches 0, a maximum diminution of $J_{1,2} \approx 46\%$ can be estimated for conversion of a diene to a diene–$Fe(CO)_3$ complex in which the H_1–H_2 dihedral angle is held constant at 0°. Significant torsion about the C_1–C_2 bond in the complexes would further decrease J_{12}. Thus it would appear that the observed trends in the ${}^3J$ couplings (Table I) roughly favor a diene–$Fe(CO)_3$ complex structure wherein H_1 and H_2 are coplanar.

More substantial evidence in support of this conclusion is obtainable from inspection of the four-bond J's in the table. There is essentially no variation in ${}^4J_{1,3}$ between the planar olefin models as compared to the corresponding iron complexes: ${}^4J_{1,3}$(**2**) = 1.0 *vs.* ${}^4J_{1,3}$(**5**) = 1.4 Hz; ${}^4J_{1,3}$(**3**) (cor) = 1.1 *vs.* ${}^4J_{1,3}$(**6**) = 1.2 and ${}^4J_{1,3}$(**7**) = 1.1. The close similarity of the ${}^4J_{1,3}$ couplings among these five compounds is in accord with the notion that a four-bond J between H atoms in a planar "W" orientation is primarily σ in character (iii above). By analogy to the angular dependency of ${}^4J$ noted by Manatt, *et al.*[7] (for couplings of type ${}^4J_{1,3}$ in **1**), as well as by Barfield and Garbisch (four-bond allylic J's)[12a,17] one can estimate that for the diene iron complexes the value of ${}^4J_{1,3}$ will approach 0 Hz at an H_1–H_3 twist angle of ~30°. Finally, the behavior of ${}^5J$ and ${}^2J$ upon diene complexation to $Fe(CO)_3$, decrease in ${}^5J_{1,4}$ by ~80% and increase in ${}^2J_{1,1'}$ by ~50%, are indicative of an extensive loss of π contribution to J_{net} upon complex formation.

Based upon the above considerations we feel that the best structural description of a diene–$Fe(CO)_3$ complex is provided by structure A in which all the C and H atoms are coplanar. In addition these π complexes seem to provide an excellent empirical test of pmr coupling theory.[18]

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(14) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2871 (1963).

(15) (a) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960), **50**, 3133 (1969); (b) M. Barfield and J. J. Reed, *ibid.*, **51**, 3039 (1969); (c) M. Barfield, *ibid.*, **48**, 4463 (1968); (d) M. Barfield and B. Chakrabarti, *J. Amer. Chem. Soc.*, **91**, 4346 (1969); (e) A. V. Cunliffe, R. Grintner, and R. K. Harris, *J. Magn. Resonance*, **3**, 299 (1970); (f) M. Bacon and G. E. Maciel, *Mol. Phys.*, **21**, 257 (1971); (g) W. J. Van Der Hart, *ibid.*, **20**, 399 (1971).

(16) See discussion in ref 7 *vs.* ref 15e,f.

(17) M. Barfield, *J. Amer. Chem. Soc.*, **93**, 1066 (1971).

(18) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

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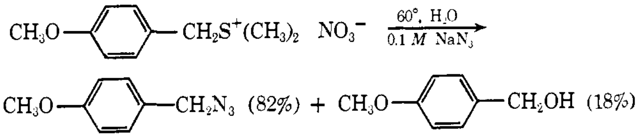
Evidence for a Unifying Mechanism of Nucleophilic Substitution into Sulfonium Ions[1]

Sir:

We wish to report that borderline behavior has now been observed in the competitive substitutions by solvent water and added nucleophile into benzyldimethylsulfonium ion (I^-, 140°, H_2O) and into *p*-methoxybenzyldimethylsulfonium ion (N_3^-, 60°, H_2O). Thus, for example, in the presence of 0.1 *M* NaN_3, an aqueous solution of *p*-methoxybenzyldimethylsulfonium nitrate (0.0066 *M*) at 60° furnishes 82% *p*-methoxybenzyl azide and 18% *p*-methoxybenzyl alcohol at a rate 1.82 times that observed in the absence of azide ion (Table I). It can readily be shown[2] that an SN2 model would predict a rate enhancement of a factor of (82/18) + 1 = 5.55 and that an SN1 model would predict a factor of 1.00.[3]



While kinetic behavior is obviously borderline, the ratio of products, $[ArCH_2N_3]/[ArCH_2OH]$, is a linear function of azide ion concentration from $[N_3^-] = 0.03$ to 0.12 *M*, with slope $m = 48.0 \pm 1.0$ (Table I).

These data are of course reminiscent of those which led us to propose[2] the ion-pair mechanism for substitution into alkyl halides and sulfonates and an analogous scheme, in which an ion-dipole assemblage, [ArC^{+}-

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(1) Supported in part by the National Science Foundation.

(2) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362, 6041 (1969).

(3) Pertinent entries of Table I establish that salt effects are minimal at these concentrations and that solvolysis rates are independent of the concentration of sulfonium salt and of the nature of the nonnucleophilic anion. Rates and products were determined by titrating liberated acid as a function of time. The stoichiometry of acid production permits an evaluation of product distribution as alkyl azide formation is not accompanied by the liberation of acid.