Figure 2. Decay curves of DNO, N_2O, and NO after photolysis: $\triangle$, m/e 30 (NO^+); $\square$, m/e 32 (DNO^+); $\bigcirc$, m/e 44 (N_2O^+).

anism of Strausz and Gunning[5] (eq. 1 and 2), which predicts

$$[DNO]^{-1} = [DNO]_0^{-1} + \frac{2k_1k_2[H_2]}{k_1 + k_2[H_2]}t \qquad (4)$$

A peak height–concentration relationship is known for N_2O but not for DNO. However, if we assume that during the decay period, following the turning off of the light (Figure 2), the DNO reacts solely to form N_2O, we can use the stoichiometry to establish a relation between the change in peak height and concentration of DNO. With this admittedly crude calibration, we have constructed second-order plots according to (4); the slopes are pressure sensitive, in agreement with (4). We are at present studying this pressure dependency, but from our present results and the form of (4) we can state that $k_1 \geq 5.6 \times 10^{-15}$ cm.^{3} molecule^{-1}/sec.$^{-1}$.

F. C. Kohout, F. W. Lampe
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania

spectrometer.[11,12] Hence, for this case

$$\log\frac{[A]}{[A]_0} = \frac{\lambda}{2.303}t \qquad (3)$$

and the decay plot is as shown by the dotted line, where λ, the leak rate constant, was determined previously. The data for m/e 44 show, however, that for about the first 20 sec. N_2O is being formed, in addition to leaking through the pinhole. After this, the straight-line behavior characteristic of change solely by pinhole leakage is observed. The behavior of m/e 32 is quite different. It is apparent that DNO disappears by a process much more rapid than leakage through the pinhole. Furthermore, the minimum in the m/e 32 curve shows that DNO is essentially gone at $t \sim$ 20 sec. when m/e 44 begins the normal pinhole leakage behavior. The minimum and subsequent rises of m/e 32 are due to the contribution to this peak of $N^{14}O^{18+}$. During photolysis [NO] is depleted, as shown in Figure 1. However, when the light is turned off diffusion of NO from the reservior containing NO, H_2, and Hg occurs until [NO] is uniform throughout. This is shown by the rise of m/e 30 in Figure 2. This interpretation was confirmed by examination of the 32/30 peak height ratio over this time interval. This ratio at first fell very sharply, while DNO was reacting, but then subsequently rose and reached a constant value.

The behavior of m/e 32 and 44 in Figures 1 and 2 shows quite clearly that DNO is the precursor of N_2O. Moreover, a reasonably linear plot of the reciprocal of the peak height of m/e 32 *vs.* time (for $t < 20$ sec.) after the photolysis was stopped indicates the DNO disappears to form N_2O in a reaction that is second order in [DNO]. This is in agreement with the mech-

Measurement of the Inversion Rate of a Secondary Amine and Its N-Deuterio Analog by Nuclear Magnetic Resonance Spectroscopy[1]

Sir:

2,2,3,3-Tetramethylaziridine (I) was first synthesized by Closs and Brois,[2] who reported that the n.m.r. spectrum of this compound "showed a single, sharp resonance line at 217 c.p.s. (relative to external benzene at 40 Mc.), thus revealing the equivalence of the four methyl groups."

Using the same method of preparation, we obtained I in pure form (as indicated by gas chromatography), having the same physical constants and infrared absorption bands as reported,[2] but showing in its n.m.r. spectrum *two* sharp peaks of equal intensities, at τ 8.88 and 8.72, respectively (at room temperature, in CCl_4, relative to internal tetramethylsilane at 60 Mc.). This separation of the chemical shifts of 6,6 methyl protons at room temperature was demonstrated in the spectra of solutions of 1 in several aprotic solvents as well as in the spectrum of the pure compound; however, it could be best studied in CCl_4 and DMF solutions at approximately 25% concentration of I. The compound is extremely hygroscopic; when its solution in CCl_4 was allowed to stand for a few minutes exposed to air, the two n.m.r. signals coalesced into a single, broader peak. This was obviously due to H_2O-catalyzed proton exchange. The same phenomenon was observed in the presence of trace amounts of alcohol or other substances having exchangeable hy-

(1) This work was supported, in part, by Public Health Service Research Grant No. CA-06695 from the National Cancer Institute.
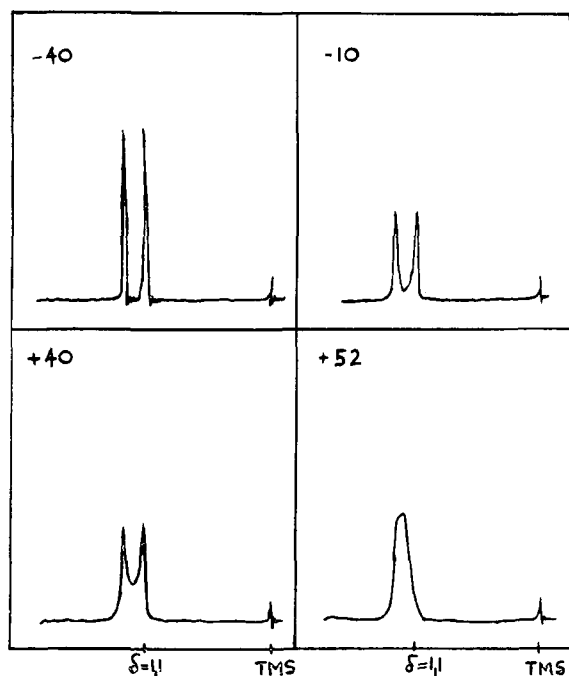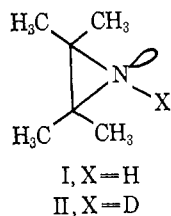(2) G. L. Closs and S. J. Brois, *J. Am. Chem. Soc.*, 82, 6068 (1960).

Figure 1. Variation of the n.m.r. spectrum of I (25%, in CCl_4) with temperature.

Figure 2. Plot of log $1/\tau\delta\omega$ as a function of $1/T$ (°K.) for compounds I and II.

drogens. The previous authors' failure to detect the two resonance peaks might have been caused by the presence of a trace amount of moisture in their sample.

I, X = H
II, X = D

Since the magnetic environment of the two methyl groups above the plane of the aziridine ring of I is different from that of the two methyl groups below the plane, one could expect to observe a difference in their chemical shifts, provided that the inversion of the nitrogen is sufficiently hindered. Such was indeed found to be the case for several N-substituted aziridines which had been studied previously[3,4]; however, the present paper reports what we believe to be the first example of a *secondary* amine having an inversion rate sufficiently slow to allow direct measurement by n.m.r. spectroscopy.

After thorough drying over solid sodium hydroxide, the two resonance lines of I (in CCl_4 solution) are separated at $-40°$ by 11 c.p.s. ($\sim\delta\omega_\infty$). On heating, this separation gradually narrows (Figure 1), and the two peaks coalesce at $+52°$ (T_c). At this temperature, the calculated[3] lifetime (t) in one conformation is approximately 0.04 sec., with the corresponding inversion rate (k') of 25 sec.$^{-1}$.

Change of the concentration of I (in CCl_4 solution), from 25 to 3%, did not result in any measurable change of peak separation at a given temperature ($+30°$). This fact indicates that hydrogen bonding could not

play an important role in the temperature dependence of the n.m.r. spectrum within this concentration range. It also minimizes the possible importance of a bimolecular proton exchange reaction ($>N_AH_A + H_BN_B< \rightleftarrows >N_AH_B + H_AN_B<$) in our carefully dehydrated system, since such reaction (catalyzed or not) would be concentration dependent. In view of the aforementioned dramatic effect of even a trace amount of water, some contribution of a catalyzed exchange reaction to the measured inversion rate might be expected,[5] and it is possible that a *small* contribution of this type of reaction escaped detection due to the limitations of accuracy of our n.m.r. measurements. However, the actual inversion rate cannot be larger than the measured value, and the latter should be considered, at least, as the maximal inversion rate.

The activation energy of inversion can be relatively easily calculated since the numbers of exchanging nuclei in the two environments are equal, and the resonance line widths are small (1 c.p.s.) compared to the chemical shift between nuclei in the two environments.[6,7] From the observed separations of the two resonance lines ($\delta\omega_e$) at various temperatures between 40 and 50° in CCl_4, the maximum separation ($\delta\omega_\infty$), and the line width ($2/T_2$), we could establish the corresponding values of $1/\tau\delta\omega$, a temperature-dependent term related to the inversion rate.[8] A plot of log ($1/\tau\delta\omega$) vs. $1/T$ (°K.) $\times 10^3$ (Figure 2, I) yields a value of 11.0 kcal./mole for E_a. Using an alternative method,[4,9] E_a was calculated from the ratios of maximum to minimum (in CCl_4) between 40 and 52°; this gave a value of 11.9 kcal./mole.

(3) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, 80, 5203 (1958).
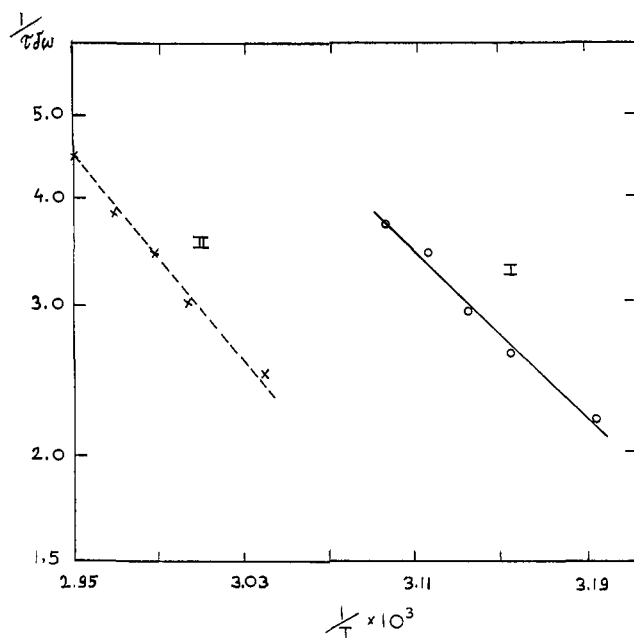(4) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, 82, 3599 (1960).

(5) R. A. Ogg, Jr., *Discussions Faraday Soc.*, 17, 215 (1954).
(6) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956).
(7) C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Am. Chem. Soc.*, 79, 6136 (1957).
(8) The notations and definitions of the terms are the same as used in ref. 6, which gives the basis and method of these calculations. However, τ is the average lifetime of the proton in each conformation, as in ref. 7.
(9) A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, 27, 1067 (1957).

In order to study the inversion of a secondary amine in which the hydrogen is replaced by a deuterium, II was prepared by equilibration of I in D_2O, followed by salting out with NaOD, distillation from solid NaOD, and subsequent storage over solid NaOD. Compound II showed the same n.m.r. spectrum at room temperature (in CCl_4) as I, but the coalescence of the two resonance lines occurred only at 68°. Using the same two alternative methods of calculation as in the case of I, the activation energy of inversion was found 14.3 (from Figure 2, II) and 15.0 kcal./mole, respectively. These results are in agreement with the expected greater inertia of an N–D bond in its vibration through the plane of the ring, due to the greater mass of the deuterium.

Thomas J. Bardos, Csaba Szantay, C. Krishna Navada
Department of Medicinal Chemistry, School of Pharmacy
State University of New York at Buffalo, Buffalo, New York
Received August 30, 1965

The Crystal and Molecular Structure of $MoS_6C_6H_6$

Sir:

Recently[1-3] the first members of a class of neutral and charged transition metal complexes $M(S_2C_2H_2)_n^{-z}$ ($n = 2$ or 3, $z = 0, 1, 2$) of the hitherto unknown ligand dithioglyoxal have been reported, which are the important basic members of a large family of metal com-
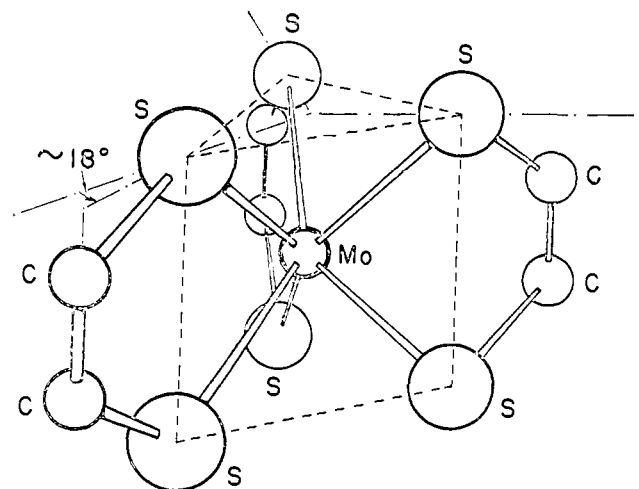

Figure 1. Schematic drawing of $[(HCS)_2]_3Mo$.

plexes of α-dithiodiketonic and of related bidentate sulfur donor ligands. The neutral tris complexes[4] are of

(1) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).
(2) H. Hoyer and W. Schroth, *Chem. Ind.* (London), 652 (1965).
(3) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, 1464 (1965).
(4) (a) G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Angew. Chem.*, **76**, 715 (1964); *Angew Chem. Intern. Ed., Engl.*, **3**, 639 (1964); (b) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964); (c) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965); (d) R. B. King, *ibid.*, **2**, 641 (1963).

particular interest since the recent X-ray analysis[5] of $Re(S_2C_2Ph_2)_3{}^{4a}$ revealed an unexpected prismatic structure. In addition it was concluded[5] from X-ray powder patterns that $Re(S_2C_2Ph_2)_3$ is isomorphous with the tungsten compound, but apparently not with the analogous and mutually isomorphous V, Cr, and Mo complexes. Independently, we have also observed that the phenyl substituted V, Cr, and Mo complexes are not isomorphous with the Re compound, but we also find the tungsten compound to be isomorphous with the latter group of compounds, while distinctly different from the Re complex.[6] Although there exists supporting evidence[5,7] suggesting prismatic structures for the majority of the tris complexes, a rigorous proof is necessary, especially since the X-ray powder patterns of the isomorphous complexes $MoS_6C_6H_6$ and $WS_6C_6H_6$ were also found to be *definitely different* from those of $ReS_6C_6H_6$.[8] In the present communication we report the results of an X-ray structural analysis of the unsubstituted molybdenum complex,[3] $MoS_6C_6H_6$. In addition to the reasons stated above, the structure of this complex is interesting as it represents the first example of a compound containing dithioglyoxal units.

Limited three-dimensional data $(hk0)-(hk3)$ (layers of Weissenberg) plus $(h0l)$ precession data were taken at $-157°$ with Zr-filtered Mo radiation. A spherical crystal was used. The unit cell is hexagonal: $a = 7.632$, $c = 11.53$ Å., $Z = 2$, space group $P6_{3/m}$. The structure was solved using two-dimensional Patterson projections to locate the Mo, S, and C atoms. The refinement was carried out by least squares using the three-dimensional data. The Mo atoms are at the special positions $(^2/_3, {}^1/_3, {}^1/_4)$ and $(^1/_3, {}^2/_3, {}^3/_4)$, and the S and C atoms in a trigonal prismatic arrangement (Figure 1) around the Mo atoms, with symmetry C_{3h}. The carbon atoms are not in the plane passing through the Mo and S atoms but deviate 18° from this plane. The Mo–S distance is 2.33 Å. (±0.02), in good agreement with the value found in MoS_2, which also has trigonal prismatic coordination.[9] The S–C distance is 1.70 (±0.03) and the C–C 1.34 Å. (±0.04). The S–Mo–S angle is 82.5° and the S$\cdots$S distance within the ligands is 3.10 Å. The distance between adjacent sulfur atoms related by the threefold axes is 3.11 Å. The molecules are relatively close-packed; in fact, the distance C–H$\cdots$S between adjacent molecules is less than the sum of the van der Waals radii. The isotropic temperature factors are all quite low and of reasonable magnitude; the R factor at present is 0.11 and further refinement with more extensive data is in progress. With the exception of the deviation of the C atoms from the S–M–S plane, the bond distances and angles are in good agreement with those found by Eisenberg and Ibers for Re-$(S_2C_2Ph_2)_3$, albeit this molecule has D_{3h} symmetry.

(5) R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 3776 (1965), and private communication prior to publication.
(6) The fact that the complexes of Cr, Mo, and W (with $S_2C_2Ph_2$ ligands) are isomorphous has been observed previously: G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 1080 (1964).
(7) E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 4012 (1965).
(8) NOTE ADDED IN PROOF. In the meantime we have also obtained well-resolved X-ray powder diagrams of $VS_6C_6H_6$, $RuS_6C_6Ph_6$, and $OsS_6C_6Ph_6$. Tris(dithioglyoxal)vanadium is not isomorphous with the Mo, W, and Re compounds. The phenyl-substituted complexes of Ru and Os both gave different powder patterns, not identical with those of the V, Cr, Mo, W, and Re compounds.
(9) R. Dickinson and L. Pauling, *J. Am. Chem. Soc.*, **45**, 1466 (1923).