

Figure 1. The structure of (TTF)(HgCl₃). The $y = 0.0$ projection illustrates the polymeric HgCl species and ring-over-bond TTF columns, while the $y = 0.5$ projection shows the Hg₂Cl₆ units and eclipsed TTF dimers. Short Cl...S contacts, one in each layer, are noted.

in this columnar array is approximately of the ring-over-bond type found in (TTF)(TCNQ)⁶ and many of its derivatives. The mean separation of molecular planes is on the order of 3.6 Å and is considerably longer than that observed in (TTF)(TCNQ) (3.48 Å)⁶ but similar to the eclipsed columnar spacings found in (TTF)Cl_{0.92} (3.59 Å)⁷ and (TTF)Br_{0.79} (3.57 Å).⁸

The second of these layers (centered about $y = 0.5$) contains solely dimeric species, Figure 1. The chloromercurate(II) entity is a dimeric, edge-shared bitetrahedron with Hg-Cl bond lengths of 2.600 (5) and 2.696 (5) Å for the bridging ligands and 2.368 (5) and 2.381 (5) Å for the terminal ligands. Coupled with these inorganic dimers are pairs of TTF⁺ cations strongly associated about centers of symmetry, Figure 1. The mean separation in these organic dimers is short at 3.43 Å (vide supra) and the molecular overlap is nearly eclipsed with a slight lateral shift. This spacing is identical with that found in the dimeric salt (TTF)Br_{1.0}.⁹

Clearly, **1** is unusual on account of the presence in one crystal of both dimeric and polymeric HgCl units and of two types of TTF aggregates. Ring-over-bond columns are observed in partially oxidized TTF derivatives, i.e., TTFⁿ⁺ ($n < 1$),^{2,6-8} while eclipsed dimers have been reported in the fully oxidized derivatives (TTF)Br⁹ and (TTF)Cl² in which $n = 1$. The x-ray data thus imply that **1** contains TTF in two different oxidation states.¹⁰

We have previously reported that the ν_3 mode in TTF undergoes large frequency shifts on oxidation of the thiocarbon to the +1 and +2 states.³ The resonance Raman spectrum of **1**, obtained using 4579-Å excitation, Figure 2, reveals two bands in a 1:1 ratio at 1415 and 1424 cm⁻¹ which we believe reflects the presence of two different kinds of TTF moieties, distinguished by a small difference in degree of charge transfer, which is consistent with the crystallographic data. Such a splitting has not been observed in numerous other metallo-

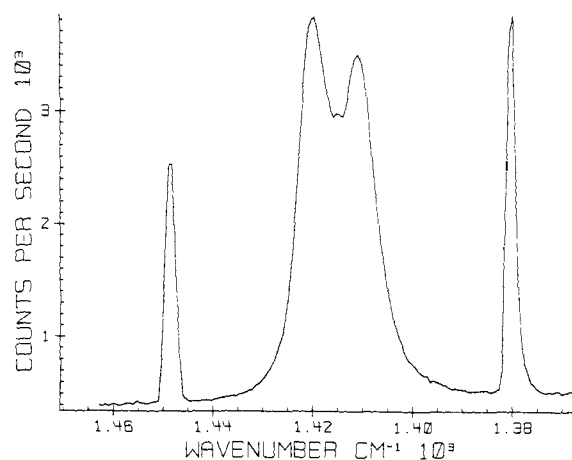


Figure 2. Resonance Raman spectrum of powdered (TTF)(HgCl₃).

tetraethylenes studied in these laboratories. These results suggest that resonance Raman spectroscopy will be useful in probing subtle features of electron distribution in charge-transfer salts.

References and Notes

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- (10) It is difficult to express this difference quantitatively but it may be estimated to be $< 0.2e$.
- (11) Address correspondence to the Central Research Laboratories, 3M Co., St. Paul, Minn. 55101.

T. J. Kistenmacher,* M. Rossi, C. C. Chiang

Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland 21218

R. P. Van Duyne,* T. Cape

Department of Chemistry and Materials Research Center
Northwestern University
Evanston, Illinois 60201

Allen R. Siedle*¹¹

Inorganic Chemistry Section
National Bureau of Standards
Washington, D.C. 20234

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Powerful Anchimeric Effect of the *N*-Nitroso Group

Sir:

We wish to report the exceptionally powerful neighboring-group effect of the *N*-nitroso group in the solvolysis of derivatives of β -hydroxydialkyl nitrosamines.

In an earlier study, we¹ reported the very rapid rate of hydrolysis of the urea functionalities in α -ureidonitrosamines.

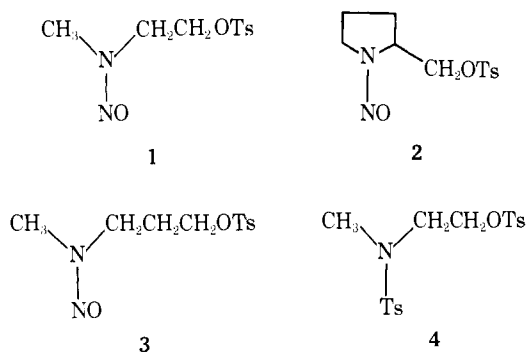
Table I. Acetolysis of Methyl-(β -tosyloxyethyl)-*N*-nitrosamine

k (s ⁻¹) $\times 10^4$	T , °C (± 0.1)	No. of runs
1.66 \pm 0.05	15	3
2.90 \pm 0.1	20	3
4.86 \pm 0.2	25	3
9.03 \pm 0.3	30	3
15.4 \pm 0.6	35	4
16.6 \pm 1.1	40	5

$\Delta H^\ddagger = 17.0$ kcal/mol, $\Delta S^\ddagger = -16.6$ eu

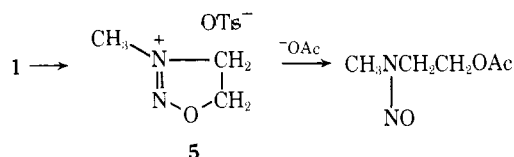
We ascribed that to the neighboring-group effect of the *N*-nitroso group. A little later, Swern and co-workers² noted that the rapid rate of hydrolysis of *N*-nitroso-2-(methylamino)acetonitrile was probably due to participation by oxygen of the *N*-nitroso group.

In order to test this effect in a more clear-cut system, tosylates **1**–**4** were prepared.³



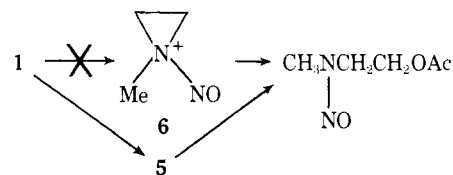
Solvolyses of these tosylates were carried out in glacial acetic acid, containing 0.08 M potassium acetate. The solutions were 0.04 M in the tosylates. At set intervals, aliquots of the solvolysis solution were withdrawn and titrated with standard perchloric acid in acetic acid. The end points were detected potentiometrically. The first-order rate plots for **1** were linear to 80% completion and then tended to level off. The rate constants were calculated using a least-squares program.

The solvolysis of **2** was too rapid to measure at 25 °C by our technique; the reaction was completed in ~ 30 s. Tosylate **3** showed no detectable solvolysis after 90 min at 25 °C. Likewise, the *N*-tosyl-*O*-tosylate **4** showed no reaction after 4 h at 25 °C. Tosylate **1**, however, solvolyzed at a convenient rate. The rate constants, together with the activation parameters, are listed in Table I. The data in Table I indicate an exceptionally fast solvolysis for a primary tosylate. At 40 °C, for example, the $t_{1/2}$ for the reaction is 7 min. The low activation energy and the large negative entropy of activation suggest participation of the *N*-nitroso group in the solvolysis. This hypothesis was strengthened even further when we found that warming of the tosylate **1** in methylene chloride resulted in the formation of **5** in essentially quantitative yield. Remarkably, **5** is reasonably stable in aqueous solution,⁴ although it reacts with a variety of nucleophiles.⁵



It is curious, in view of the high reactivity of **1** and **2**, that the next higher homologue **3** is very unreactive under these conditions. The apparent large difference in the rates of solvolysis suggests that the transition state leading to the six-membered-ring analogue of **5** is more difficult to attain, presumably because the entropy change, associated with the loss

of additional degrees of freedom of the three-carbon chain, is more unfavorable. By the same token the extremely fast solvolysis of **2** is facilitated by the rigidity of the ring system. The inertness of **4**, under our reaction conditions, underlines the obligatory nature of the *N*-nitroso group participation. However, since **4** is not a nitrosamine, it is an imperfect model, because the stereoelectronic environment of the nitrogen in this molecule is different from that of the tosylate **1**. Thus, the lack of reactivity of **4** does not necessarily prove that it is not the amino nitrogen of **1**, rather than the oxygen of the nitroso group, which is responsible for the rate enhancement. That the *N*-nitrosoaziridium ion, **6**, is not the cyclic intermediate is



shown unambiguously by the infrared spectra of several nitrosamines, including **1** and its precursor alcohol. Nitrosamines, in general, show a strong band at ~ 1450 cm⁻¹. This is the N–O stretch.⁶ While this stretch in **6** ought to be found at a higher wavenumber (because of the increased force constant of the N–O bond), the infrared spectrum of the cyclized intermediate showed no prominent bands in the 1400–1800-cm⁻¹ region.

These data may have considerable bearing on the question of the mechanism of carcinogenicity of β -hydroxylated nitrosamines.⁷ These nitrosamines can be formed by enzymatic oxidation of dialkylnitrosamines (where alkyl > C₂) and they are also found in the environment.⁸ According to the present data, it seems entirely possible that a sulfate or a phosphate conjugate of a β -hydroxyalkylnitrosamine could serve as a direct-acting, in vivo, alkylating agent. Biological experiments to test this hypothesis are being carried out.

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References and Notes

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- The tosylates were prepared from the corresponding alcohols and tosyl chloride, using pyridine as the base (R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944)). The temperature was not allowed to go above 5 °C, and the standard workup was conducted rapidly using cold solvents. The initial oily products were filtered through a short silica column. The tosylates crystallized nicely from the eluate (ether). The NMR spectra and mass spectrometric and elemental analyses were completely consistent with the assigned structures.
- The NMR spectrum of **5**, taken in D₂O or Me₂SO-*d*₆ on a 60-MHz instrument, shows ring resonances shifted downfield relative to **1**; i.e., the ethyldine protons of **5** show an AA'BB' pattern centered on 5.1 ppm as opposed to an almost degenerate resonance at 4.4 ppm in **1**, while the methyl group resonance (singlet) shifts from 3.0 ppm in **1** to 4.2 ppm in **5**. The tosyl group resonances are shifted upfield slightly in **5** relative to **1**.
- The cyclic intermediate **5**, as well as the tosylate **1**, react with thiols and with guanine or guanosine to give substitution products. These results will be reported shortly. In the solvolysis system, the principal product (>90% yield) is the corresponding acetate.
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C. J. Michejda,* S. R. Koepke

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588

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