cyanate ion, was evaporated to dryness, yielding 485 mg (97%) of **4**, mp 149–152°.

B. In Other Solvents. The thermal stability of **3** was examined at the boiling point of common organic solvents as follows. A sample of 5 mg of **3** was heated in 1 ml of boiling solvent. At intervals of 1, 2, 5, 15, and 30 min, after adjusting the volume of the solution for evaporation, 2 drops of the solution were removed and tested for the presence of thiocyanate ion with 1 drop of 5% FeCl₃ solution. The results are summarized as follows: in methylene chloride (bp 42°), no conversion was noted after 30 min; in chloroform (bp 61°) and in methanol (bp 65°) only trace conversion of **3** to **4** was noted after 30 min; in CH₃CN (bp 81°) and in ethylene chloride (bp 83°) maximum intensity was noted after 5 min (no **3** detectable by TLC); and in dioxane (bp 102°) maximum intensity was noted after 1 min (no **3** detectable by TLC).

C. At Its Melting Point. A 5-ml beaker containing 100 mg of **3** was slowly increased in temperature on a hot stage. Samples (∼1 mg) were removed at 60, 80, 100, and 120° and were tested for the presence of thiocyanate ion with 5% FeCl₃ solution, all giving negative results. At 135–140°, the sample melted and was completely converted to **4** as indicated by ir, TLC, and a positive FeCl₃ test.

1-(*N*-Benzoylthiocarbamoyl)pyrrolidine (7). To 1.00 g (6.13 mmol) of **2** in 5 ml of CH₃CN was added dropwise with cooling and stirring 0.88 g (12.4 mmol) of pyrrolidine. The mixture was stirred in an ice bath for 0.5 hr, filtered, and washed with CH₃CN. The colorless solid was collected and recrystallized from CH₃CN to give 0.48 g (34%) of 1-(*N*-benzoylthiocarbamoyl)pyrrolidine as colorless needles: mp 133–134°; ir 3100 (NH), 2960 (CH), 1642 (C=O), 1603, and 1530 cm⁻¹; NMR (DMSO-*d₆*) δ 1.93 (m, 4, 2 CCH₂), 3.67 (m, 5, 2 CH₂N + NH), 7.63 (m, 3, *o*- and *p*-ArH), and 8.00 (m, 2, *m*-ArH).

Anal. Calcd for C₁₂H₁₄N₂OS: C, 61.51; H, 6.02; N, 11.96; S, 13.68. Found: C, 61.55; H, 6.02; N, 12.06; S, 13.55).

As anticipated,[7] the compound failed to react with ammoniacal silver nitrate solution to give a black precipitate of silver sulfide and its *S*-methyl derivative did not release methyl mercaptan on attempted hot alkaline hydrolysis.

Registry No.—**1**, 1779-81-3; **2**, 532-55-8; **3**, 55103-06-5; **4**, 55103-07-6; **5**, 55103-08-7; **7**, 55103-09-8; **9**, 29146-60-9; **10**, 6558-36-7.

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(13) Infrared spectra were taken on a Beckman IR-5 spectrophotometer in KBr pellets unless otherwise indicated, and NMR spectra were determined on a Varian Associates T-60A spectrometer. Mass spectra were obtained at 70 eV and 290° on an LKB spectrometer. Uv spectra were taken on a Beckman DB-G recording spectrophotometer. Melting points were determined on a Fisher-Johns apparatus and are uncorrected.

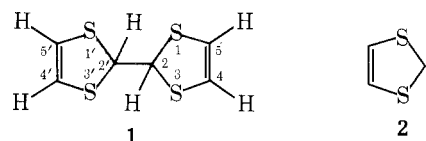## Reduction of the 1,3-Dithiolium Cation with Hexacarbonylvanadate(1−)

A. R. Siedle* and R. B. Johannesen

While the reduction of 1,2-dithiolium cations has been extensively studied,[1-4] less information is available concerning the isomeric 1,3-dithiolium salts. An electrochemical reduction of the 2-thioethoxy-4,5-dithiomethoxy-1,3-dithiolium cation to the orthothiooxalate has been reported.[5] We wish to report a reductive coupling of the unsubstituted 1,3-dithiolium cation using sodium (bisdiglyme) hexacarbonylvanadate(1−) as the reducing agent. This is, to our knowledge, the first example of the use of V(CO)₆⁻ as a reducing agent for organic compounds.

When solutions of 1,3-dithiolium hexafluorophosphate[6] and Na(diglyme)₂V(CO)₆ in acetone–tetrahydrofuran were mixed and the resulting solution diluted with water, white, crystalline 2,2′-bi(1,3-dithiolyl) (**1**) separated; the very air-sensitive V(CO)₆ was not isolated in this procedure.[7] The mass spectrum of **1** was characterized by strong M⁺ and M⁺/2 peaks. The 220-MHz ¹H NMR spectrum of **1** in acetone-*d₆* consisted of two singlets at δ 4.73 and 6.20 in a 1:2 ratio. At 60 MHz, with a resolution better than 0.4 Hz, these signals showed unresolved fine structure.[8] Examination of the ¹³C satellites in the ¹H NMR spectrum of **1** revealed $^3J_{H(4)H(5)} = 5.4 \pm 1$ Hz and $^3J_{H(2)H(2')} = 10.5 \pm 1$ Hz. The former value is similar to $^3J_{H(3)H(4)}$ in aromatic derivatives such as pyrrole and furan.[9] The latter coupling constant is larger than might be expected for vicinal protons but might be modified by the presence of the electronegative sulfur atoms or by a preference by **1** for a specific conformation. The ¹³C NMR spectrum of **1** in carbon tetrachloride consisted of two doublets at 115.6 ($J_{CH} = 184$ Hz) and 60.3 ppm ($J_{CH} = 160$ Hz) [relative to internal (CH₃)₄Si] in a 2:1 intensity ratio.

The formation of **1** presumably proceeds through a one-electron reduction by V(CO)₆⁻ of the 1,3-dithiolium cation to form the free radical **2**. Subsequent dimerization of **2** would then lead to **1**.

Experimental Section

A solution of 0.33 g (1.44 mmol) of C₃H₃S₂⁺PF₆⁻ in 10 ml of 1:1 acetone–tetrahydrofuran was added with stirring to 0.75 g (1.44 mmol) of Na(C₆H₁₄O₃)₂V(CO)₆[10,11] in 15 ml of the same solvent. The solution turned dark and a small amount of gas was evolved. The mixture was evaporated to ca. 5 ml on a rotary evaporator. Slow addition of water caused the product to separate as white flakes which were further purified by sublimation (90°, 10⁻³mm). The yield was 0.09 g (59%), mp 150–151°. Anal. Calcd for C₆H₆S₄: C, 34.95; H, 2.91; S, 62.14. Found: C, 35.18; H, 3.04; S, 61.95. Ir (KBr) 3030 (w), 2950 (w), 1580 (w), 1525 (m), 1500 (w), 1245 (m), 1165 (s), 1075 (w), 855 (w), 780 (s), 730 (m), 695 (m), 435 (w), and 315 cm⁻¹ (m); uv (C₂H₅OH) λ_max (log ε) 290 (3.23) and 309 nm (3.22); mass spectrum (70 eV) *m/e* (assignment, rel abundance) 208 (¹²C₆¹H₆³²S₃³⁴S, 4.9), 206 (M⁺, 27), 103 (M⁺/2, 100), 45 (HCS⁺, 25).

A mixture of 0.05 g of 2,2′-bi(1,3-dithiolyl), 0.1 g of active manganese dioxide, and 3 ml of acetonitrile was gently refluxed for 3 hr to give a yellow solution. Preparative thin layer chromatography (1:1 benzene–hexane, silica gel) afforded 0.013 g (26%) of tetrathiafulvalene, identified by its R_f and ultraviolet spectrum.

Registry No.—**1**, 51187-35-0; hexacarbonylvanadate(1−), 20644-87-5; 1,3-dithiolium cation, 288-75-5; 1,3-dithiolium hexafluorophosphate, 55298-73-2.
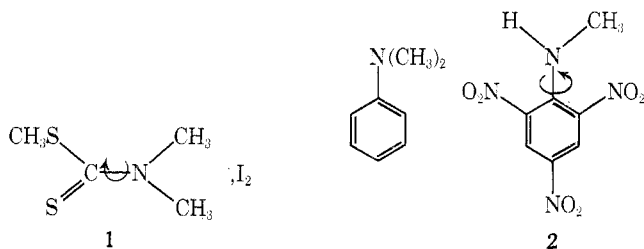
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(7) If the reaction is run in water, 1 and V(CO)₆, identified by its infrared spectrum, precipitate. However, the yield of 1 under these conditions is only 25%.
(8) The ¹H NMR spectrum of 1 should be an A₂XX'A'₂ pattern. The ¹H NMR spectrum of C₃H₃S₂⁺PF₆⁻ in acetone shows resonances at δ 11.72 (t, 1 H, ⁴JHCSCH = 2 Hz) and 9.58 (d, 2 H, J = 2 Hz). This suggests that JAX in 1 will be ~2 Hz and that JAA' will be ≪2 Hz. In fact, the ¹³C satellite spectrum indicates that all long-range couplings are <0.5 Hz.
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(11) Certain commercial equipment or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Internal Rotation of Charge-Transfer Complexes[1]

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We report here a study of torsional barriers to rotation about single bonds of charge-transfer complexes. Despite wide theoretical[3] and biological[4] interest in charge-transfer complexes, there have been few previous measurements of the effect of such association on internal rotation.[5] Two systems were investigated. Internal rotation rates were determined about the central nitrogen–carbon bond of *N,N*-dimethyldithiocarbamic acid methyl ester (1) in the presence and absence of an *acceptor*, I₂. Rotation rates were also determined about the nitrogen–aryl bond of *N*-methyl-2,4,6-trinitroaniline (2) in the presence and absence of a *donor*, *N,N*-dimethylaniline. Charge-transfer complexes of 1 with I₂ and 2 with *N,N*-dimethylaniline fall into the "n–aσ" [3,6] and "bπ–aπ" [3] classifications, respectively.

1

2

Rotation rates of 1 were evaluated by ¹H NMR lineshape analysis of the singlet-to-doublet transition of the *N*-methyl signal. Selection of 1 for this work was based on two considerations. First, the *N*-methyl signal coalesces near room temperature (38°). This precluded the need to attain high temperatures (where complexes dissociate) or low temperatures (where evaluation of the static NMR parameters is difficult). An even more important reason for choosing 1 stemmed from the sizable association constant found for 1 and I₂ (K_{assoc} = 222 M^{-1} at 25.0° in chlorobenzene). Favorable binding is necessary to obtain kinetic effects sufficiently large to interpret meaningfully. There is evidence that I₂ complexes with 1 at the thiocarbonyl site[7].

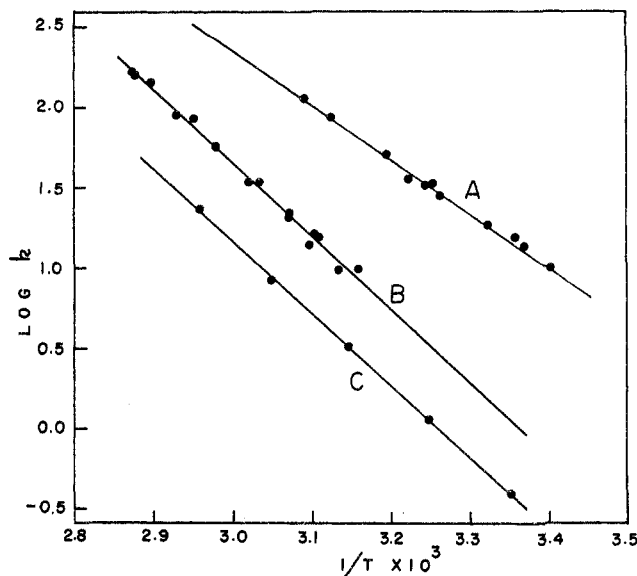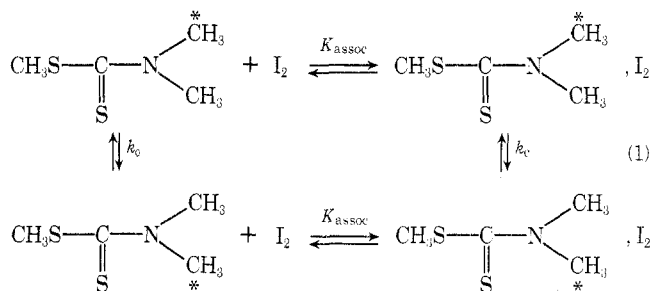**Figure 1.** Line A: Arrhenius plot of log k_{obsd} (sec⁻¹) vs. the reciprocal of the temperature (K) for rotation of 1 in chlorobenzene in the absence of I₂. Line B: Arrhenius plot of log k_{obsd} vs. 1/T for rotation of 0.100 M 1 and 0.208 M I₂ in chlorobenzene. Line C: Arrhenius plot of log k_c (see eq 1) vs. 1/T.

Rates of internal rotation of 0.100 M 1 in chlorobenzene at several temperatures between 21 and 51° (Figure 1, line A) afforded the following activation parameters: $\Delta G^{\ddagger}_{298}$ = 15.88 kcal/mol,[8] $\Delta H^{\ddagger}$ = 15.1 kcal/mol, and $\Delta S^{\ddagger}$ = −1.4 eu. Doubling the concentration of 1 had no effect on the rate constants. When 0.208 M I₂ was added to the solution, the rate of internal rotation[9] decreased (as manifested, for example, by elevation of the coalescence temperature from 38 to 61°). A plot of log k_{obsd} vs. 1/T is given in Figure 1, line B. The observed rate data could also be analyzed in terms of the scheme shown in eq 1. In order to extract k_c (the rate

$$\text{(1)}$$

of internal rotation of the complex itself), it was necessary to evaluate K_{assoc} using a spectrophotometric method based on the Ketelaar equation.[10,11] K_{assoc} was found to equal 222 ± 1 M^{-1} at 25.0° and 62.9 ± 1 M^{-1} at 55.0°.[12] Thus, 96.1% of 1 exists in the complexed state at 0.100 M 1 and 0.208 M I₂ at 25.0°. Values of C (the concentration of complex) and k_0 (the rotation rate in the absence of I₂) were inserted into eq 2 to obtain k_c values at several temperatures.[13] We find that k_0 is 37 times greater than k_c at 25.0°, indicating that complexation with I₂ retards rotation. An Arrhenius plot of k_c is shown in Figure 1, line C. From this plot we estimate that $\Delta G^{\ddagger}_{298}$ = 18.1 ± 0.1 kcal/mol; *this is 2.2 kcal/mol greater than that of the uncomplexed substrate.*[14]

$$k_{obsd} = k_0 \left(\frac{[1]_0 - [C]}{[1]_0} \right) + k_c \left(\frac{[C]}{[1]_0} \right) \quad \text{(2)}$$

Rotation rates about the bond joining the amine nitrogen to the aryl group in *N*-methyl-2,4,6-trinitroaniline (2) were