References and Notes

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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 ^{1}H NMR spectrum of **1** should be an A$_2$XX'A'$_2$ pattern. The ^{1}H NMR spectrum of $C_3H_3S_2^+PF_6^-$ in acetone shows resonances at δ 11.72 (t, 1 H, $^4J_{HCSCH}$ = 2 Hz) and 9.58 (d, 2 H, J = 2 Hz). This suggests that J_{AX} in **1** will be ~2 Hz and that $J_{AA'}$ will be ≪2 Hz. In fact, the ^{13}C satellite spectrum indicates that all long-range couplings are <0.5 Hz.
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(10) This material was obtained from Pressure Chemical Co., Pittsburgh, Pa.
(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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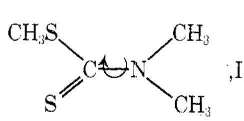
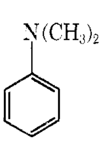
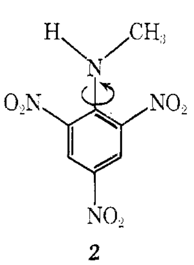
We report here a study of torsional barriers to rotation about single bonds of charge-transfer complexes. Despite wide theoretical[3] and biological[4] interest in charge-transfer complexes, there have been few previous measurements of the effect of such association on internal rotation.[5] Two systems 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*, I_2. 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 I_2 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 ^{1}H 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 I_2 ($K_{\text{assoc}} = 222\ M^{-1}$ at 25.0° in chlorobenzene). Favorable binding is necessary to obtain kinetic effects sufficiently large to interpret meaningfully. There is evidence that I_2 complexes with 1 at the thiocarbonyl site[7].

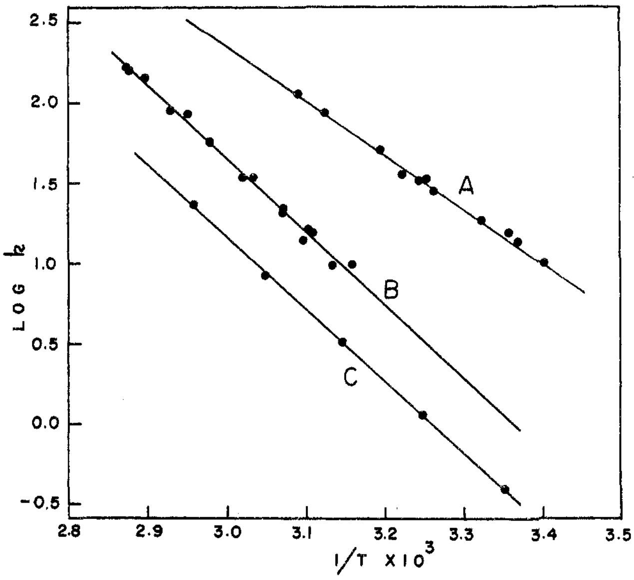
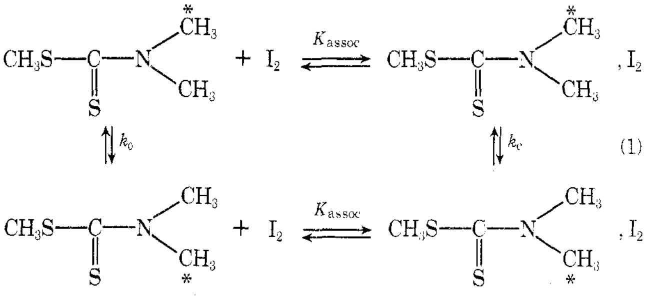


Figure 1. Line A: Arrhenius plot of log k_{obsd} (sec^{-1}) vs. the reciprocal of the temperature (K) for rotation of 1 in chlorobenzene in the absence of I_2. Line B: Arrhenius plot of log k_{obsd} vs. $1/T$ for rotation of 0.100 M 1 and 0.208 M I_2 in chlorobenzene. Line C: Arrhenius plot of log k_c (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 I_2 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 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 I_2 at 25.0°. Values of C (the concentration of complex) and k_0 (the rotation rate in the absence of I_2) 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 I_2 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]



(1)

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

Rotation rates about the bond joining the amine nitrogen to the aryl group in *N*-methyl-2,4,6-trinitroaniline (2) were determined from the NMR line shape of the aryl proton signals. Two experimental problems hampered the study of rotation of 2 when complexed with *N,N*-dimethylaniline: (1) low temperatures were necessary to bring rotation of **2** within the NMR time scale (T_c of aryl protons = −55° in acetone) and (2) the complex has a relatively small association constant ($K_{assoc} = 2\ M^{-1}$ at −60° in acetone). It was therefore not possible to analyze the kinetics in terms of eq 1. However, we did establish that the effect of π–π complexation is small. When 57% of 2 is complexed, the rotation rate increases only twofold (barely larger than the experimental error).

In summary, we have found that n–σ complexation of 1 to an acceptor decreases its rate of rotation, whereas π–π complexation of 2 to a donor causes only a small rate perturbation. These findings bear on the controversial question of whether weak donor–acceptor complexes are primarily stabilized by electron transfer ("charge-transfer" model[15]) or by van der Waals forces ("electrostatic" model[16–18]). On the basis of our results with the π–π complex of **2**, we can conclude that either electron transfer between the π donor and π acceptor is insignificant or else electron transfer does not appreciably affect internal rotation in the acceptor. The latter appears unlikely, especially in view of the claim that a small degree of charge transfer can have a large effect on vibrational spectra and other properties.[19] A firm decision between the possibilities must, of course, await theoretical calculations. Electron transfer is more probable in the complex between 1 and I_2, because, according to the parameters of Drago and Wayland,[20] both the donor and acceptor possess strong charge-transfer properties. Since $\Delta G^\ddagger$ for rotation of 1 is insensitive to a wide range of protic and aprotic solvents,[8] nonspecific medium effects (including hydrogen bonding) have little affect on rotation. Therefore, actual electron transfer is a likely cause of the modified rotational barrier.

Experimental Section

Materials. *N,N*-Dimethyldithiocarbamic acid methyl ester (1) and *N*-methyl-2,4,6-trinitroaniline (2) were preppared according to published procedures.[21,22] Chlorobenzene was distilled over P_2O_5 and again over K_2CO_3.

Kinetics. Rate constants for rotation were calculated with the aid of an RCA Spectra 70/55 computer which adjusts τ (the reciprocal of $2k_{obsd}$) so as to minimize deviations between experimental and theoretical spectral parameters.[23] NMR spectra were recorded with a Jeol JNM-MH-100 spectrometer equipped with a variable-temperature probe. Temperatures, calculated by the equation of Van Geet,[24] were measured before and after each run and are believed to be accurate to ±0.5°. Six to eight spectra were traced in both directions at each temperature, and the resulting rate constants were averaged. An optimum constant homogeneity was achieved by adjusting the resolution control prior to each run while observing the SCH_3 signal. This peak also provided an estimate of the effective relaxation times (T_2's). Spectra were obtained using a sweep width of 54 or 108 Hz, sweep time of 250 sec, filter band width of 10 Hz, and radiofrequency field of 0.1 mG.

Registry No.—1, 3735-92-0; **2**, 1022-07-7; I_2, 7553-56-2; *N,N*-dimethylaniline, 121-69-7.

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(12) These values correspond to $-\Delta H$ = 8.2 kcal/mol and $-\Delta S$ = 16.7 eu. The thermodynamic parameters in another solvent, CCl_4, are reported to be $-\Delta H$ = 7.53 kcal/mol and $-\Delta S$ = 15.3 eu.[7]
(13) We also performed a series of runs using 0.198 *M* **1** and 0.301 *M* I_2 with no significant difference in results.
(14) The rate data were not considered sufficiently precise to calculate $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (which are difficult to obtain by NMR methods even in simple systems).
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