

## Solvent Effects on Strong Charge Transfer Complexes

### II. *N,N*-Dimethylthioformamide and Iodine in Nonpolar and Polar Solvents

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The strong charge transfer complex between *N,N*-dimethylthioformamide and iodine has been studied in the ultraviolet and visible regions in the solvents heptane, carbon tetrachloride, dichloromethane, and acetonitrile, and in the visible region in dioxane and ethanol. Thermodynamic and spectral data for the 1:1 complex in these solvents are reported. In carbon tetrachloride and dioxane, both the equilibrium constant and the enthalpy of formation  $-\Delta H^\circ$  were smaller than in heptane. In dichloromethane and acetonitrile, the equilibrium constant was much higher than in the hydrocarbon, but a corresponding increase in  $-\Delta H^\circ$  was not observed. The position of the maximum for the charge transfer band was closely the same, except in acetonitrile, where a blue shift from 302  $m\mu$  in heptane to 294  $m\mu$  was detected. The results are discussed in view of current approaches for correlating variation in solvent properties with changes in thermodynamic and spectral characteristics for donor-acceptor complexes. The infrared spectrum of the complex was found to give strong evidence for complexation with iodine at the sulfur atom.

The influence of the solvent on the thermodynamic and spectral characteristics of charge transfer (*CT*) complexes has attracted considerable interest. In the system trimethylamine-sulfur dioxide, the energy and free energy values for all the interaction and solvation steps relating to the formation of the complex in the gas phase and in heptane was recently reported.<sup>1</sup> The study demonstrated that even in an "inert" solvent, the reacting species are in states which are energetically very different from the gas phase. The large contribution of solvation to the thermodynamic properties of the three species (donor, acceptor, and the complex) indicates that the equilibrium constants and heats of formation for the complexes may be expected to vary considerably from gas to a nonpolar solvent, and from one nonpolar solvent to another. In polar solvents, this situation should presumably be even more pronounced.

The thermodynamic data reported for *CT* complexes both in the only "inert solvent", the gas phase, and in solution, indicate some trends. For the weak and intermediate strength complexes, the equilibrium constant decreases and the heat of formation decreases or remains nearly constant when going from gas to a nonpolar solvent.<sup>2</sup> A similar situation seems to prevail when the medium is changed from a nonpolar to a polar solvent.<sup>3-5</sup> In contrast, for the strong complex between trimethylamine and sulfur dioxide, both  $K_c$  and  $-\Delta H^\circ$  were larger in heptane than in the gas phase,<sup>1</sup> and a further stabilization in dichloromethane and chloroform was observed.<sup>6</sup> Increased polarity of the solvent has also been found to favour the formation of some strong iodine complexes.<sup>5,7,8</sup>

In continuation of a program concerned with the effect of solvents on strong *CT* complexes, we have obtained the ultraviolet and visible spectra and the thermodynamic characteristics of the complex between iodine and *N,N*-dimethylthioformamide [ $\text{H}-\text{C}(\text{S})-\text{N}(\text{CH}_3)_2$ ]. The heat of formation for a few complexes between thioamides and iodine have been reported<sup>8-10</sup> and shows that these compounds are strong donors. *N,N*-Dimethylthioformamide (DMTF) was chosen because this substance and its iodine complex are sufficiently soluble in nonpolar and polar solvents. The solvents were heptane, carbon tetrachloride, dioxane, dichloromethane, ethanol, and acetonitrile. Studies in the gas phase were not feasible with our present equipment.

## EXPERIMENTAL

*Chemicals.* *N,N*-Dimethylthioformamide was synthesized from dimethylformamide and  $\text{P}_2\text{S}_5$ .<sup>11</sup> The raw product was distilled four times under reduced pressure; b.p. 97°/12 mm. (Found: C 40.43; H 7.77; N 16.07; S 35.96. Calc. for  $\text{C}_3\text{H}_7\text{NS}$ : C 40.41; H 7.91; N 15.71; S 35.96). The infrared<sup>12</sup> and NMR<sup>13,14</sup> spectra were identical with the published spectra. The solvents heptane, carbon tetrachloride, and dichloromethane, all *Uvasol* from Merck, were dried carefully. Absolute ethanol was distilled three times from magnesium shavings and iodine crystals in a nitrogen atmosphere. Dioxane, and the solvents carbon disulfide, tetrachloroethylene, and benzene used in the infrared measurements were *p.a.* quality from Merck, and were used without further purification.

*Instrumental.* The ultraviolet and visible spectra were recorded with a Beckman DK-1 recording spectrophotometer, equipped with a thermostatted cell holder. As a check, a Zeiss PMQ II spectrophotometer was also used for some of the measurements. A pair of matched cells, 1 cm long, was employed. The infrared spectra were recorded on a Perkin Elmer model 21 instrument, with sodium chloride optics. Below 650  $\text{cm}^{-1}$ , a Beckman IR-9 instrument was used. The solvents were carbon disulfide (4000–1700  $\text{cm}^{-1}$  and 1400–650  $\text{cm}^{-1}$ ), tetrachloroethylene (1700–1400  $\text{cm}^{-1}$ ), and benzene (500–300  $\text{cm}^{-1}$ ). The perturbations of some bands were also studied in dichloromethane. The cell thickness varied between 0.5 and 2.0 mm, and a variable cell filled with the solvent was used in the reference beam.

*Preparation and stability of the solutions.* Stock solutions of DMTF were prepared by weighing into a 100 ml volumetric flask, and by subsequent dilution of this solution to 100 ml when very dilute solutions were needed. Stock solutions of iodine were made up by weight. Mixed solutions were prepared by pipetting into 25 ml volumetric flasks.

In the solvents heptane, carbon tetrachloride, dioxane, and dichloromethane, the mixed solutions were stable for at least 24 h. No indications for the formation of  $\text{I}_3^-$  by irreversible chemical reactions or by transformation from an outer to an inner complex<sup>15</sup> were observed. In acetonitrile some  $\text{I}_3^-$  was formed with time, as inferred from the absorption bands at 290 and 360  $\mu\mu$ , particularly when the solutions were not protected against light. The spectra in this solvent were recorded with very fresh solutions. Some  $\text{I}_3^-$  was formed when iodine was dissolved in ethanol, and on addition of DMTF,

the amount of the polyhalide ion increased rapidly. In water DMTF and iodine reacted immediately and no *CT* band was observed. The infrared spectra of the mixed solutions did not change over a period of hours.

*Methods of calculation.* The equilibrium constants were determined from the absorption data for a series of mixed solutions using a modified Lang equation<sup>9</sup>

$$\frac{C_A \cdot C_D \cdot l}{E^\circ - E_A - E_D} = \left( C_A + C_B - \frac{E^\circ - E_A - E_D}{l(\epsilon_C - \epsilon_A - \epsilon_D)} \right) \frac{1}{\epsilon_C - \epsilon_A - \epsilon_D} + \frac{1}{K(\epsilon_C - \epsilon_A - \epsilon_D)} \quad \text{I}$$

$C_A$  and  $C_D$  are the initial acceptor and donor concentrations, respectively,  $E_A$  and  $E_D$  the corresponding absorbances for these species, and  $E^\circ$  the measured total absorbance.  $\epsilon_C$ ,  $\epsilon_A$ , and  $\epsilon_D$  are the molar extinction coefficients, and  $l$  the cell length in cm. An iteration procedure, based upon a preliminary guess of  $\epsilon_C$ <sup>9</sup> was programmed for the IBM 1620 II, which also calculated the standard errors in the equilibrium constants and extinction coefficients for the complex. In heptane, carbon tetrachloride, dichloromethane, and acetonitrile, the value of  $K_c$  was determined from the ultraviolet studies. Since the corrections for donor absorption are essential,  $\epsilon_D$  was carefully determined, and also the slight variation with temperature. The equilibrium constants were obtained in the 320–350  $m\mu$  region, because DMTF absorbs strongly at shorter wavelengths.  $K_c$  values obtained from the data at 320, 330, and 340  $m\mu$  were in good agreement.  $\Delta H^\circ$  for the complex was determined in the usual way from the temperature variation of  $K_c$  by a least squares treatment. The temperature intervals were 10–40° for heptane and carbon tetrachloride, 10–25° for dichloromethane, and 10–35° for acetonitrile. The concentration regions for DMTF were (M): heptane,  $1.2 \times 10^{-4}$  to  $1.8 \times 10^{-3}$ ; carbon tetrachloride,  $1.5 \times 10^{-4}$  to  $3.5 \times 10^{-3}$ ; dichloromethane,  $6.0 \times 10^{-5}$  to  $6.6 \times 10^{-4}$ ; acetonitrile,  $3.5 \times 10^{-5}$  to  $3.1 \times 10^{-4}$ . The iodine concentrations were between  $3 \times 10^{-5}$  and  $5 \times 10^{-5}$  for the various sets of measurements. The concentrations were corrected for the thermal expansion of the solvents.

In dioxane  $K_c$  was determined with the aid of eqn. 1 from the blue shifted iodine band at 410  $m\mu$ , since the *CT* absorption for the dioxane-iodine complex prevented calculations from absorbances in the ultraviolet region. The donor concentrations varied between  $3.7 \times 10^{-4}$  and  $3.0 \times 10^{-3}$  M, and the iodine concentration was  $3.8 \times 10^{-4}$  M. The  $\Delta H^\circ$  value in this solvent was determined by the "enthalpy method",<sup>16</sup> In ethanol,  $I_3^-$  absorption introduced too great uncertainties in the  $K_c$  values to yield reliable data for  $\Delta H^\circ$ . However,  $K_c$  at 20° was determined from the visible absorption data.

Table 1. Thermodynamic parameters with standard deviations for the *N,N*-dimethylthioformamide-iodine complex.

Solvents	$d^a$	$K$ (20°C) (M <sup>-1</sup> )	$\Delta G^\circ$ (20°C) (kcal/mole)	$\Delta H^\circ$ (kcal/mole)	$\Delta S^\circ$ (e.u.)
Heptane	1.9	1850 ± 30	-4.36	-10.3 ± 0.3	-20.1 ± 0.6
Carbon tetrachloride	2.2	1270 ± 60	-4.15	-7.8 ± 0.3	-12.4 ± 1.1
Dioxane	2.2	610 ± 15	-3.72	-8.3 ± 0.3	-15.6 ± 0.7
Dichloromethane	9.1	6400 ± 90	-5.09	-10.1 ± 0.3	-17.0 ± 0.9
Ethanol	24.3	2270 ± 80	-4.48	<sup>b</sup>	<sup>b</sup>
Acetonitrile	38.8	27700 ± 2100	-5.94	-10.1 ± 0.6	-14.3 ± 1.8

<sup>a</sup> Dielectric constant. <sup>b</sup> Not obtained.

## RESULTS

The *CT* band of the complex was observed as a strong and broad band with maximum around 300  $m\mu$ . Job's method of continuous variation<sup>18</sup> was applied in the solvents carbon tetrachloride and dichloromethane, and the

1:1 stoichiometry of the complex was demonstrated. By the procedure explained in the experimental section  $K_c$  was determined at different temperatures. The  $K_c$  values at 20°C and the calculated thermodynamic functions  $\Delta H^\circ$  and  $\Delta S^\circ$  are collected in Table 1, together with the standard errors. Due to systematic errors, and the rather narrow temperature range, the accuracy in  $\Delta H^\circ$  is certainly not as good, and we feel that uncertainties of 0.5 kcal/mole for heptane and carbon tetrachloride and 1.0 kcal/mole for dichloromethane, dioxane, and acetonitrile are more reliable estimates.

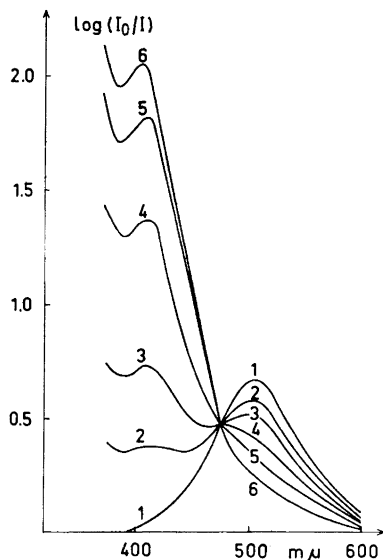


Fig. 1. Visible absorption spectrum of *N,N*-dimethylthioformamide and iodine ( $7.281 \times 10^{-4}$  M) in dichloromethane at 20°C, 1 cm cell. The concentrations (M) of DMTF are 1) zero; 2)  $1.282 \times 10^{-4}$ ; 3)  $2.566 \times 10^{-4}$ ; 4)  $5.123 \times 10^{-4}$ ; 5)  $7.698 \times 10^{-4}$ ; 6) the constructed blue shift band.

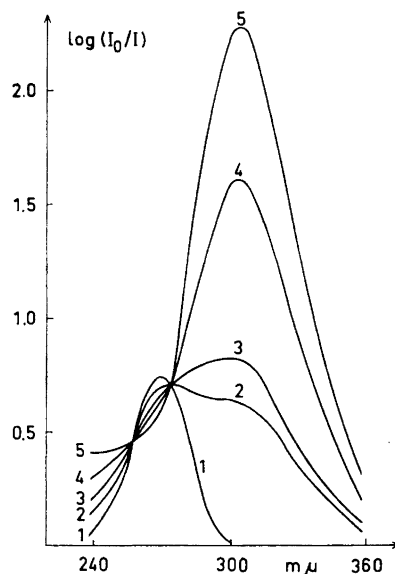


Fig. 2. Ultraviolet spectrum of *N,N*-dimethylthioformamide ( $4.801 \times 10^{-5}$  M) and iodine in dichloromethane at 20°C, 1 cm cell. The concentrations (M) of iodine are: 1) zero; 2)  $0.706 \times 10^{-4}$ ; 3)  $1.059 \times 10^{-4}$ ; 4)  $4.413 \times 10^{-4}$ ; 5) the constructed charge transfer band.

The ultraviolet spectrum in dichloromethane is shown in Fig. 2. At constant DMTF and varying iodine concentration isosbestic points appear at 273 and 259  $m\mu$ . The latter probably arises from overlap between the  $\pi \rightarrow \pi^*$  band in the free donor and the corresponding blue shifted band in the complex. The position of the *CT* maximum was determined by adding to the reference cell the amount of free DMTF calculated from the  $K_c$  values. Correction for the absorbance of free iodine was not necessary. The results are given in Table 2, together with the extinction coefficients at the *CT* maximum. In heptane and dichloromethane the half band widths  $\Delta\nu_{\frac{1}{2}}$  could be determined on both sides of the *CT* maximum. The *CT* band in these solvents was found to be symmetrical within the experimental errors. For the other solvents, only

Table 2. The spectral characteristics of the *CT* band of the *N,N*-dimethylthioformamide-iodine complex in various solvents.

Solvent	$\lambda$ ( $m\mu$ )	$\epsilon_C$ ( $10^{-4} M^{-1} cm^{-1}$ )	$\Delta\nu_{\frac{1}{2}}$ ( $10^{-3} cm^{-1}$ )	$f$	$D$ (Debye)
Heptane	302	$4.1 \pm 0.2$	5.8	1.03	8.0
Carbon tetrachloride	304	$4.7 \pm 0.2$	6.0	1.22	8.9
Dioxane	305	$5.9 \pm 0.4$	5.4	1.38	9.5
Dichloromethane	302	$4.8 \pm 0.3$	6.2	1.28	9.1
Acetonitrile	294	$5.4 \pm 0.4$	5.2	1.22	9.1

the long wavelength side could be studied. The oscillator strength, calculated from Tsubomura and Lang's formula, assuming symmetrical bands in all solvents, is also found in Table 2. Due to the correction for donor absorption, the extinction coefficients and  $f$ -values have rather large uncertainties, but the position of the *CT* maximum are considered accurate to within 2  $m\mu$ .

*The blue shifted (BS) iodine band.* The position of the iodine visible band in the solvents employed varied between 521  $m\mu$  in heptane to 436  $m\mu$  in ethanol. When DMTF was added to a solution of iodine in one of the solvents, the intensity of this band decreased, and a new band appeared in the visible region assigned as the *BS* band of iodine in the complex. In all solvents except acetonitrile and ethanol this band had a distinct maximum, but in acetonitrile only a plateau around 400  $m\mu$  was observed. Constant iodine concentration and varying donor concentration gave isosbestic points, supporting the assumption that only one complex, most probably of 1:1 stoichiometry, is formed as was found from the Job plots. For dichloromethane, this is illustrated in Fig. 1. The isosbestic point was at 474  $m\mu$  and the *BS* maximum at 406  $m\mu$ . Since there is considerable overlap between the *CT* and *BS* bands, the real *BS* maxima are at a somewhat longer wavelength than the values given in Table 3. The extinction coefficients at the tabulated *BS* maxima also have a considerable contribution from the *CT* band.

*Infrared spectra.* The infrared spectra of DMTF have been reported.<sup>12</sup> When iodine was added to a solution of DMTF, some distinct spectral changes took place, including both band displacements and intensity changes. These

Table 3. Spectral characteristics of the blue shifted iodine band of the *N,N*-dimethylthioformamide-iodine complex in various solvents.

Solvent	$\lambda_{I_2}^a$ ( $m\mu$ )	IBP <sup>b</sup> ( $m\mu$ )	$\lambda_{BS}$ ( $m\mu$ )	$\epsilon$ ( $M^{-1}cm^{-1}$ )	$\Delta\lambda$ ( $m\mu$ )	$f$	$D$ (Debye)
Heptane	521	491	436	$2950 \pm 100$	85	<sup>c</sup>	<sup>c</sup>
Carbon tetrachloride	516	488	428	$3020 \pm 70$	88	0.046	2.0
Dioxane	450	471	411	$2950 \pm 40$	39	0.066	2.4
Dichloromethane	503	474	406	$2840 \pm 40$	97	0.058	2.2

<sup>a</sup>  $I_2$  in pure solvent. <sup>b</sup> Isosbestic point. <sup>c</sup> Not obtained.

changes were most pronounced for the strong band at  $1537\text{ cm}^{-1}$  (dichloromethane) which was shifted to  $1570\text{ cm}^{-1}$  and intensified in the complex. A large shift to lower wave numbers was observed for the  $968\text{ cm}^{-1}$  band (from  $968\text{ cm}^{-1}$  to  $937\text{ cm}^{-1}$  in dichloromethane). The medium strong band at  $1123\text{ cm}^{-1}$  ( $\text{CS}_2$ ) was shifted to  $1131\text{ cm}^{-1}$ . Bands at  $901\text{ cm}^{-1}$  and  $514\text{ cm}^{-1}$  were also perturbed, but for the other bands, no larger shifts than  $3\text{ cm}^{-1}$  were detected. The infrared spectra of the *N,N*-dimethylthioacetamide—iodine complex have been reported not obtainable because of decomposition of the solutions.<sup>10</sup>

## DISCUSSION

*Location of the donor site.* Arguments based upon thermodynamic evidence,<sup>5,9</sup> NMR spectra,<sup>10</sup> and infrared shifts<sup>8,20</sup> have been presented to support the conclusion that the sulfur atom acts as the electron donor in thioamide—iodine complexes. The infrared spectrum does not provide conclusive evidence because of extensive coupling of C—N, C—S, and other vibrations. However, the changes in the infrared spectra of DMTF on S-methylation<sup>12</sup> and on complexation to iodine were found to be closely parallel. The sulfur atom, therefore, most probably, is the donor site.

*Thermodynamic results.* In attempting to explain the role of the solvent in *CT* equilibria, both specific interactions with the solvent (*via* competing chemical equilibria) and non-specific solvent effects have been considered. Trotter and Hanna<sup>21</sup> have listed several references to publications in which both types of interactions were discussed. Drago *et al.*<sup>22</sup> showed that the concept of specific interaction of the solvent benzene with iodine seemed adequate to explain the differences in  $\Delta H^\circ$  and  $K_c$  for the complex formation between dimethylacetamide and iodine in carbon tetrachloride and benzene. In dichloromethane these authors found that the specific interaction between the donor and the hydrogen bonding solvent was not sufficient to account for the difference in  $\Delta H^\circ$ , as compared with the more inert solvent. It was concluded that the complex was stabilized to the extent of about  $-1\text{ kcal/mole}$  by unspecific solvation in dichloromethane relative to carbon tetrachloride. In the systems investigated in this study, specific interactions take place between iodine and the solvents dioxane, acetonitrile, and ethanol. The thermodynamic constants for these complex formation reactions, measured in an inert solvent, have been reported. Also specific interactions between DMTF and the solvents are conceivable, but even if the necessary data were available, we would not attempt to use the "competing equilibrium" approach for more principal reasons. In our opinion, it is not very fruitful to explain solvation effects by considering the solvent as a chemical reactant, and introducing mass action relations explicitly involving the concentration of the solvent. Since it is always necessary to vary considerably the solvent activity in order both to infer the stoichiometry and thermodynamic constants of the postulated solvent-solute equilibria, one can never achieve an unequivocal separation of the effects of specific solute-solvent interactions from non-specific effects on the activity coefficients of the solutes. The only association reactions in solution for which thermodynamic data can be obtained in an

unambiguous way are these in which solvated solutes combine to give solvated complexes, all species being in the limit dissolved at infinite dilution.

An alternative method for correlating solvent effects on molecular complexes has been proposed by Christian *et al.*<sup>23,24</sup> In this approach, it is postulated that a fraction  $\alpha$  of the total internal energy or Gibbs free energy of solvation for donor and acceptor is retained by the complex, independent of temperature or solvent, at least in the absence of strong specific interactions. The single empirical constant  $\alpha$  was shown to be adequate for correlating the effects of several solvents on hydrogen bonding equilibria,<sup>23,24</sup> and was also used with reasonable success for the trimethylamine-sulfur dioxide complex in the gas phase and in heptane.<sup>1</sup> It was emphasized<sup>1</sup> that by this solvent correlation method, complexes could be classified into those which are favoured by reactive solvents ( $\alpha > 1$ ) and those which are not, ( $\alpha < 1$ ). The thermodynamic results obtained in heptane and dichloromethane, however, may not seem compatible with this approach. The formation constant is much higher in the latter solvent, which means that the free energy of solvation for the complex relative to heptane is significantly greater than the sum of the donor and acceptor solvation free energies. The parameter  $\alpha$  therefore is larger than 1 when the Gibbs free energy of solvation is concerned. Since  $\alpha$  then is supposed to be greater than 1 also regarding heats of solvation, a more negative  $\Delta H^\circ$  should be expected for the complex in dichloromethane. This, however, was not confirmed experimentally. As reflected in the formation constants the complex is strongly favoured by polar solvents, even when competing equilibria between solute and solvent are involved. The increase in  $-\Delta H^\circ$ , which we expected in these solvents according to the arguments given above, has, however, not been verified. Recently, Lang<sup>5</sup> also reported a large increase in  $K_c$  for the tetramethylthiourea-iodine complex in dichloromethane relative to heptane, without a corresponding increase in the heat of formation, although the error limits for  $\Delta H^\circ$  were quite large.

However, in the strong complexes, the contribution of the dative charge transfer structure to the ground state wave function is of considerable magnitude.<sup>25,26</sup> Therefore it seems reasonable that the stabilization of the complex in polar solvents is due to the increased interaction between the dipole of the donor-acceptor bond and the solvent. From this point of view, complexation should be most favoured by the most polar solvent, (acetonitrile), in agreement with observation. This explanation, which has also been proposed by Lang,<sup>5</sup> suggests that a more negative  $\Delta H^\circ$  in polar solvents than in nonpolar is the main reason for the increased formation constants. Solvent effects on other strong *CT* complexes are now being studied in this laboratory with a manual spectrophotometer,<sup>27</sup> which we hope will improve the accuracy of the heats of formation.

In dioxane, both the formation constant and heat of formation were significantly lower than in heptane. These results are in contrast to the observations for the isopropylamine-iodine complex in the same solvents.<sup>25</sup> The low value for  $K_c$  and  $\Delta H^\circ$  in carbon tetrachloride may also be due to a specific interaction between DMTF and the solvent. The intensity of the  $n-\pi^*$  transition in DMTF was considerably higher and the maximum at shorter wavelength than in heptane, indicating an interaction between the lone pair elec-

trons on sulfur and the carbon tetrachloride molecules. Electron accepting properties for this solvent have been reported.<sup>28,29</sup>

*Spectral results.* The position of the *CT* maximum was nearly the same in the solvents investigated, except for acetonitrile, where a shift from 302  $m\mu$  in heptane to 294  $m\mu$  was observed. This blue shift is opposite to what is commonly found on transfer of a weak or medium strength *CT* complex from a less polar to a more polar medium.<sup>3,5</sup> A similar trend has been reported for the strong triphenylarsine-iodine<sup>7</sup> and tetramethylthiourea-iodine<sup>5</sup> complexes. It was proposed<sup>5,7</sup> that this reversal of shifts indicated that the ground state was more than 50 % dative, corresponding to a larger dipole moment in the ground state than in the excited state. However, the contribution of the dative wave function to the ground state of the tetramethylthiourea-iodine adduct was recently estimated to 18 %, from measurements of the dipole moment.<sup>26</sup> Furthermore, for the trimethylamine-sulfur dioxide complex a blue shift of the complex band from gas to heptane and from heptane to dichloromethane was observed.<sup>1</sup> In this case, the ground state is also probably not the more dative. For this complex<sup>1</sup> it was proposed that the blue shift was due to the enhanced resonance separation of the ground and excited states, which accompanies the increase in the dative structure contribution to the ground state in the polar environment.<sup>25</sup> Since an approximate estimate, using reasonable values for the parameters,<sup>30,31</sup> indicated that also the present complex is considerably less than 50 % dative, we think that the same explanation may be valid in this case. In all the solvents, except acetonitrile, this effect is then nearly compensated by the red shift due to the interaction between the ground and excited state dipoles and the solvent.<sup>1</sup>

The oscillator strength for the *CT* band also does not show much variation. The experimental uncertainties may be too large to justify discussion, but the *f*-value in heptane is low compared to the other solvents. The larger value in dichloromethane and acetonitrile is consistent with an increased dative structure contribution to the ground state wave function, which according to Mulliken's theory leads to increased oscillator strength for the *CT* transition.<sup>32</sup>

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#### REFERENCES

1. Grundnes, J. and Christian, S. D. *J. Am. Chem. Soc.* **90** (1968) 2239, part I of this series.
2. (a) Lang, F. T. and Strong, R. L. *J. Am. Chem. Soc.* **87** (1965) 2345; (b) Goodenow, J. M. and Tamres, M. *J. Chem. Phys.* **43** (1965) 3393; (c) Kroll, M. and Ginter, M. L. *J. Phys. Chem.* **69** (1965) 3671; (d) Prochorow, J. *J. Chem. Phys.* **43** (1965) 3394; (e) Prochorow, J. and Tramer, A. *J. Chem. Phys.* **44** (1966) 4545; (f) Tamres, M. and Goodenow, J. M. *J. Phys. Chem.* **71** (1967) 1982; (g) Kroll, M. *J. Am. Chem. Soc.* **90** (1968) 1097; (h) Duerksen, W. D. and Tamres, M. *J. Am. Chem. Soc.* **90** (1968) 1379.
3. Plahte, E., Grundnes, J. and Klæboe, P. *Acta Chem. Scand.* **19** (1965) 1897.
4. Drago, R. S., Bolles, T. F. and Niedzielski, R. J. *J. Am. Chem. Soc.* **88** (1966) 2717.



5. Lang, R. P. *J. Phys. Chem.* **72** (1968) 2129.
6. Grundnes, J. and Christian, S. D. *Acta Chem. Scand.* **23** (1969) 3583.
7. Augdahl, E., Grundnes, J. and Klæboe, P. *Inorg. Chem.* **4** (1965) 1475.
8. Bhaskar, K. R., Bhat, S. N., Murthy, A. S. N. and Rao, C. N. R. *Trans. Faraday Soc.* **62** (1966) 788.
9. Lang, R. P. *J. Am. Chem. Soc.* **84** (1962) 1185.
10. Niedzielski, R. J., Drago, R. S. and Middaugh, R. L. *J. Am. Chem. Soc.* **86** (1964) 1694.
11. Willstätter, R. and Wirth, T. *Ber.* **42** (1909) 1908.
12. Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **20** (1966) 597.
13. Walter, W. and Maerten, G. G. *Ann.* **669** (1963) 66.
14. Loewenstein, A., Melera, A., Rigny, P. and Walter, J. J. *J. Phys. Chem.* **68** (1964) 1597.
15. Bhat, S. N. and Rao, C. N. R. *J. Am. Chem. Soc.* **88** (1966) 3216.
16. Drago, R. S., Carlson, R. L., Rose, N. J. and Wenz, D. A. *J. Am. Chem. Soc.* **83** (1961) 3572.
17. Hosoya, H., Tanaka, J. and Nagakura, S. *Bull. Chem. Soc. Japan* **33** (1960) 850; see also Sandström, J. *Acta Chem. Scand.* **16** (1962) 1616, and references cited there.
18. Job, P. *Ann. Chim. Paris* (10) **9** (1928) 113.
19. Tsubomura, H. and Lang, R. P. *J. Am. Chem. Soc.* **83** (1961) 2085.
20. Gerbier, M. and Gerbier, J. *Compt. Rend.* **B 263** (1966) 1057.
21. Trotter, P. J. and Hanna, M. W. *J. Am. Chem. Soc.* **88** (1966) 3724.
22. Drago, R. S., Bolles, T. F. and Niedzielski, R. J. *J. Am. Chem. Soc.* **88** (1966) 2717.
23. Christian, S. D., Johnson, J. R., Affsprung, H. E. and Kilpatrick, P. J. *J. Phys. Chem.* **70** (1966) 3376.
24. Johnson, J. R., Kilpatrick, P. J., Christian, S. D. and Affsprung, H. E. *J. Phys. Chem.* *In press*, and other papers in preparation.
25. Kobinata, S. and Nagakura, S. *J. Am. Chem. Soc.* **88** (1966) 3905.
26. Bhat, S. N. and Rao, C. N. R. *J. Am. Chem. Soc.* **90** (1968) 6008.
27. Rogstad, A. and Augdahl, E. *Work in progress*.
28. Ozt, J. B. and Oyler, D. E. *Trans. Faraday Soc.* **62** (1966) 2076.
29. Grechishkin, W. S. and Kyúntsel, I. A. *J. Struct. Chem. USSR* **7** (1966) 113.
30. Yada, H., Tanaka, J. and Nagakura, S. *Bull. Chem. Soc. Japan* **33** (1960) 1660.
31. Mulliken, R. S. and Person, W. B. *Ann. Rev. Phys. Chem.* **13** (1962) 103.
32. Krishna, V. G. and Bhowmik, B. B. *J. Am. Chem. Soc.* **90** (1968) 1700.

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