1.0×10^{-2} M, respectively. The rates were determined with a Unicam SP 200 G Infrared Spectrophotometer and the rate constants were reproduced with an accuracy better than ± 3 %.

Conductivity measurements. When using $\lambda^{\circ}_{Ph_4As^+} = 55.8$ ohm^{-1} cm^{-2} mol^{-1} [19] the following equivalent conductivities at infinite dilution in acetonitrile at 25 °C were found:

$\lambda^{\circ}_{(Ph_4As)_2S_4O_6} = 172$ ohm^{-1} cm^{-2} mol^{-1}
$\lambda^{\circ}_{S_4O_6^{2-}} = 60.4$ ohm^{-1} cm^{-2} mol^{-1}
$\lambda^{\circ}_{Ph_4AsCN} = 150$ ohm^{-1} cm^{-2} mol^{-1}
$\lambda^{\circ}_{CN^-} = 94.2$ ohm^{-1} cm^{-2} mol^{-1}

From the plots, λ *versus* $\sqrt{c}$, the salts appeared to be completely dissociated in acetonitrile. The conductivity measurements were performed on a conductivity meter type CD M3 with a conductivity cell, type CDC 304 (immersion type) with a cell constant 1.00 cm ± 10 %.

Acknowledgement. The author wishes to expresss his thanks to The Norwegian Research Council for Science and the Humatities for a grant.

1. Kurtenacker, A. *Z. Anorg. Allg. Chem. 116* (1921) 243.
2. Kurtenacker, A. and Goldbach, E. *Z. Anorg. Allg. Chem. 166* (1927) 177.
3. Foss, O. *Kgl. Nor. Vidensk. Selsk. Skr.* (1945) No. 2, p. 20.
4. Davis, R. E. *J. Phys. Chem. 62* (1958) 1599.
5. Foss, O. *Acta Chem. Scand. 4* (1950) 404.
6. Davis, R. E., Louis, J. B. and Cohen, A. *J. Amer. Chem. Soc. 88* (1966) 1.
7. Ritter, R. D. and Krueger, J. H. *J. Amer. Chem. Soc. 92* (1970) 2316.
8. Austad, T. *Acta Chem. Scand. A 28* (1974). *In press.*
9. Jander, G., Grüttner, B. and Scholz, G. *Chem. Ber. 80* (1947) 279.
10. Kerr, D. F. and Wilson, I. R. *J. Chem. Soc. Dalton Trans.* (1973) 459.
11. Schmidt, M. and Talsky, G. *Chem. Ber. 93* (1960) 719.
12. Austad, T., Engemyr, L. B. and Songstad, J. *Acta Chem. Scand. 25* (1971) 3535.
13. Taylor, R. P. and Kuntz, Jr., I. D. *J. Amer. Chem. Soc. 94* (1972) 7963.
14. Kolthoff, I. M. and Chantooni, Jr., M. K. *J. Amer. Chem. Soc. 90* (1968) 5961.
15. Haberfield, P., Nudelman, A., Bloom, A., Romm, R. and Ginsberg, H. *J. Org. Chem. 36* (1971) 1792.
16. McLennan, D. J. *J. Chem. Soc. B* (1966) 709.
17. Austad, T., Songstad, J. and Åse, K. *Acta Chem. Scand. 25* (1971) 331.
18. Kurtenacker, A. and Laszlo, G. *Z. Anorg. Allg. Chem. 237* (1938) 359.
19. Springer, C. H., Coetzee, J. F. and Kay, R. L. *J. Phys. Chem. 73* (1969) 471.

Received May 6, 1974.

Hydrogen Bonding of Diphenylamine. Part 1. A Near Infrared Study of Its Complexes with Some Proton Acceptors

ANTTI KIVINEN,[a] JUHANI MURTO [b] and BIRGITTA SILVENNOINEN [a]

[a] Department of Pharmacy, University of Helsinki, Fabianinkatu 35, SF-00170 Helsinki 17, Finland and [b] Department of Physical Chemistry, University of Helsinki, Meritullinkatu 1 C, SF-00170 Helsinki 17, Finland

In the literature two quite different series of equilibrium constants K_c have been reported for the hydrogen bonded complexes formed by diphenylamine (DPA) with some proton acceptors. The values of Bhowmik and Basu [1] are appreciably greater than the values obtained by Sannigrahi and Chandra [2] by the same method (UV) and in similar conditions (Table 1). The proton acceptors used in the two studies mentioned above were not the same, but their proton-accepting power should be of the same order of magnitude.

To obtain a more reliable estimate of the proton donor strength of diphenylamine, we have measured the equilibrium constants for some diphenylamine–proton acceptor complexes by the IR method.

Experimental. Chemicals. Diphenylamine (*purum* grade, Schering-Kahlbaum AG) and benzophenone (zur Synthese, E. Merck AG) were used as received. 1,4-Dioxan (Uvasol grade, E. Merck AG) and dimethyl sulfoxide (DMSO, *purum* grade, Fluka AG) were purified by fractional crystallization. Hexamethylphosphoric triamide (HMPA, zur Synthese, E. Merck AG) was boiled with calcium oxide at diminished pressure for about 15 h and then distilled through a Vigreux column (b.p. 80 °C/2 mmHg). *N,N*-Dimethylacetamide (*purissimum* grade, Fluka AG) and carbon tetrachloride (Uvasol grade, E. Merck AG) were dried with molecular sieves 4A.

Table 1. Literature values of the equilibrium constants for the hydrogen bonding of diphenylamine with proton acceptors. Method UV, solvent cyclohexane, temperature 27 °C.

Proton acceptors	K_c / M^{-1}	Ref.
Benzophenone	14.4	1
Quinoxaline	17.4	1
Diethylnitrosoamine	28.2	1
Diethyl ether	0.28	2
Dioxan	0.58	2
Tetrahydrofuran	0.40	2

Table 2. Equilibrium constants K_c and frequency shifts $\Delta\nu$NH for hydrogen bonding of diphenylamine (about 0.15 M in CCl_4) with proton acceptors. Temperature 25 °C.

Proton acceptor	K_c / M^{-1}	$\Delta\nu$NH / cm^{-1}	Concentration range/M
Benzophenone	0.622	48	0.19 – 0.49
1,4-Dioxan	0.608	73	0.54
N,*N*-Dimethylacetamide	4.18	102	0.080 – 0.125
DMSO	6.85	117	0.069 – 0.138
HMPA	19.4	155	0.054 – 0.066

Spectrometric measurements. These were carried out with a Beckman DK-2A spectrophotometer as described previously.[3,4] The concentrations were corrected for the thermal expansion of the solvent. The $\Delta\nu$-values are believed to be accurate within $\pm 3-5$ cm^{-1}, ΔH-values within ± 2 kJ mol^{-1} and K_c-values within 10 %.

The non-SI units used were: 1 M = 1 mol dm^{-3}; 1 mmHg = 133.322 Pa.

Results and discussion. The results given in Table 2 reveal that the proton donor strength of DPA is relatively low. This is to be expected, because phenyl groups reduce the basicity of amines. The values of K_c for DPA – benzophenone and DPA – 1,4-dioxan complexes are approximately equal, the frequency shift $\Delta\nu$NH being somewhat smaller in the former case. Our value $K_c = 0.608$ M^{-1} is close to the value 0.58 M^{-1} (27 °C, cyclohexane) reported by Sannigrahi and Chandra [2] for the DPA – dioxan complex. No drastic changes in spectrometric quantities are expected on going from carbon tetrachloride solutions to cyclohexane solutions, and thus we conclude that our results are in accordance with those reported by Sannigrahi and Chandra. The value $K_c = 14.4$ M^{-1} (27 °C, cyclohexane) reported by Bhowmik and Basu [1] for the DPA – benzophenone complex, on the other hand, is remarkably greater than our value $K_c = 0.622$ M^{-1} (25 °C, CCl_4). Thus it would seem that the values reported by Bhowmik and Basu for various hydrogen bonded complexes of DPA are indeed much too great.

Table 3. Spectrometric quantities for the hydrogen bonded 1:1 diphenylamine – hexamethylphosphoric triamide complex.

t / °C	K_c / M^{-1}	$-\Delta H$ / kJ mol^{-1}	$\Delta\nu$NH / cm^{-1}
0	46.1		
25	19.4	21.4	155
50	10.5		

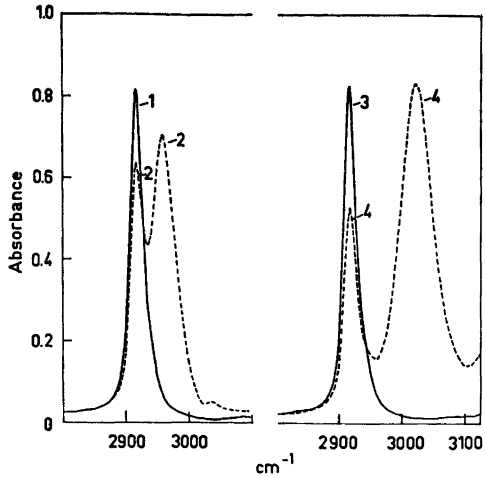

Fig. 1. Representative spectra of DPA – base systems. Solvent CCl_4, temperature 25 °C, path length 1 mm. Curve *1*, 0.148 M DPA, CCl_4 in the reference beam; curve *2*, 0.148 M DPA + 0.491 M benzophenone, 0.491 M benzophenone in the reference beam; curve *3*, 0.149 M DPA, CCl_4 in the reference beam; curve *4*, 0.149 M DPA + 0.138 M DMSO, 0.138 M DMSO in the reference beam.

The experimental data of Bhowmik and Basu are too meagre to conclude what is the reason for the discrepancies between their and our values.

The enthalpy of complexation was measured for the DPA – HMPA complex (Table 3), since HMPA is the most strongly complexing proton acceptor studied in this work. The value we obtained, $-\Delta H = 21.4$ kJ mol^{-1}, is somewhat greater than expected from the relatively small frequency shift (155 cm^{-1}); this enthalpy value indicates medium strong bonding. The values of the other thermodynamic parameters for the DPA – HMPA complex are $-\Delta G° = 7.36$ kJ mol^{-1} and $-\Delta S° = 47.1$ J mol^{-1} K^{-1}.

In Fig. 1 are shown two representative spectra of DPA complexes.

Acknowledgement. We gratefully acknowledge financial support from the Finnish National Research Council for Sciences.

1. Bhowmik, B. B. and Basu, S. *Trans. Faraday Soc. 58* (1962) 48.
2. Sannigrahi, A. B. and Chandra, A. K. *J. Phys. Chem. 67* (1963) 1106.
3. Kivinen, A. and Murto, J. *Suom. Kemistilehti B 40* (1967) 6.
4. Kivinen, A., Murto, J. and Kilpi, L. *Suom. Kemistilehti B 40* (1967) 301.

Received May 13, 1974.