

Donor Strength of *N*-Substituted Phosphoramides

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Summary The polarity, basicity, and donor strength of some *N*-substituted phosphoramides was investigated; *NN'N''*-tris(tetramethylene)phosphoramide (TPPA) was found to have a higher donor number than any other known solvent.

HEXAMETHYLPHOSPHORAMIDE has been reported to have the highest electron-donating power of all known polar aprotic solvents.^{1,2} The basicity of this compound has been attributed to the strong polarization of the P-O bond.³⁻⁵

N-Tetramethylene-*N'N''*-bis(dimethyl)phosphoramide (MPPA); *NN'*-bis(tetramethylene)-*N''*-dimethylphosphoramide (DPPA), and *NN'N''*-tris(tetramethylene)phosphoramide (TPPA) have been prepared⁶ and their donor strengths determined¹ from the heat of their complexation with SbCl_5 ($\text{DN}_{\text{SbCl}_5}$). The dipole moments were measured

in solution in benzene.⁷ The dielectric constant of pure TPPA and HMPA were also determined and the Onsager equation⁸ was used in the calculation of the dipole moment in the pure liquids.

The results of these determinations, and the refractive indices and viscosities are summarized in the Table.

It is evident from the data that the basicity and the polarity of the investigated phosphoramides increases with the replacement of the methyl groups by tetramethylene groups: HMPA \sim MPPA $<$ DPPA $<$ TPPA. The donor strength of TPPA is by 25% higher than that of HMPA. This result is consistent with the fact that pyrrolidine is a stronger base than dimethylamine. The difference between the dipole moment of pure TPPA and its value extrapolated to infinite dilution, indicates that the pure liquid is highly associated. The association of HMPA molecules was ruled out by Dubois and Viellard.⁴ However, their value of

TABLE. Donor numbers and physical constants of the phosphoramides

	$\text{DN}_{\text{SbCl}_5}^a$	ϵ_{25°	Dipole moment μ (in bulk)		$N_D^{25^\circ}$	ρ^{25° (g/cm ³)	η^{25° (cp)
			μ_{∞}^b				
HMPA	38.8 ^c	29.71	5.37	4.37	1.4553	1.021	3.10
MPPA	38.0	—	—	4.77	1.4771	1.054	4.85
DPPA	45.4	—	—	5.27	1.4968	1.088	8.56
TPPA	47.2	45.08	7.29	5.52	1.5128	1.132	19.05

^a ΔH of complexation in methylene chloride solutions. ^b In benzene solutions. ^c From ref. 1.

$\mu_{\infty} = 5.54 D$ seems to be in error. The present measurements yield a value similar to that reported by Schafer and Curran ($\mu_{\infty} = 4.30 D$).⁵

The equilibrium constant of the complexation of cobalt thiocyanate with TPPA is several orders of magnitude

larger⁹ than that of its complexes with HMPA. It should also be noted that, because of the bulkiness of the TPPA and of the DPPA molecules steric effects will be important in solution.

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