

## SOLVENT EFFECTS ON THE ELECTRIC MOMENTS OF SOME HEXAHYDRO-*s*-TRIAZINES

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### ABSTRACT

Molar polarizations and permanent electric moments of unsubstituted 1,3,5-triphenyl hexahydro-*s*-triazine (HsT) and the -methyl, -chloro, -methoxy, -ethoxy and -nitro, tri *p*-phenyl substituted derivatives of HsT have been determined in nine different solvents with permittivity range  $\epsilon_s = 1.8$  to 32.0. A positive solvent effect has been detected and the polarizability ellipsoid of the molecules envisaged. The correlation parameter ( $g$ ) values seem to linearly depend on solvent  $\epsilon_s$  and the Hammett substituent ( $\sigma_p$ ) constant values of HsT derivatives.

### INTRODUCTION

THE permanent electric moments ( $\mu$ ) and molar polarizations of unsubstituted and *p*-phenyl substituted derivatives of 1,3,5-triphenyl hexahydro-*s*-triazines (HsT) were reported earlier<sup>1</sup>. It is well known that values of  $P$  and  $\mu$  evaluated by the dilute solution method are generally solvent-dependant and differ from gas phase values<sup>2,3</sup>. For solutes like HsT and its derivatives whose decomposition inception lies between m.p and b.p range, the gas phase ( $\mu_g$ ) determinations prove difficult. The same is overcome by the extrapolation of  $\epsilon_s$  vs  $\mu_s$  plots assuming  $\mu_s \rightarrow \mu_g$  as  $\epsilon_s \rightarrow 0$ . The ratio  $\mu_s/\mu_g$  gives the correlation parameter  $g$  which is a measure of molecular interactions<sup>4,5</sup>. Data based on these lines are not available in the literature for molecules like HsT which possess certain stereochemical characteristics. Hence, a rationalization on the static dielectric data of HsT compounds in various solvents, has been presented here. Compounds of the study are: 1,3,5 [-triphenyl; -tri(-4-methyl phenyl); -tri(-4-chlorophenyl); -tri(-4-methoxy phenyl); -tri(4-ethoxy phenyl) and -tri(4-nitro phenyl)] hexahydro-*s*-triazines and the same are denoted as I, II, III, IV, V and VI respectively.

### EXPERIMENTAL

Solutes I-VI were prepared and recrystallized as mentioned elsewhere<sup>6</sup>. The solvents employed belong to spectro grade E. Merck samples. Static permittivity values were computed on a PICO-dipolmeter at 7 MHz frequency. A 10 ml capacity

pyknometer and an Abbe refractometer were used for density and refractivity studies. In all measurements 25°C was kept constant by an ultrathermostat fitted with external circulation.

### RESULTS AND DISCUSSION

#### *Correlation parameters*

Evaluation of  $g$  of the solutes I-VI needs the solute  $\mu_g$  values. Hence the dipole moment of the solute in the solution ( $\mu_s$ ) from various solvents was determined, employing Guggenheim's dilute solution method with the solute concentration ( $x_2$ ) not exceeding 0.09. Using the  $\epsilon_{1,2}$ ,  $d_{1,2}$  and  $P_1$  data, the total molar polarization of the solutes ( $P_{2\infty}$ ) was determined from the plots of  $P_2$  vs  $x_2$  as  $x_2 \rightarrow 0$ . Similarly the electronic polarization  $P_e$  was determined from the  $R_2$  vs  $x_2$  plot, as  $x_2 \rightarrow 0$ ,  $R_2 \rightarrow R_{2\infty}$  where  $R_2(\infty)$  is the total molar refraction of the solute. The induced polarization  $P_i = P_e + P_a$  where  $P_e = R_{2(\infty)}$  and  $P_a \simeq 0.15 P_e$  respectively. The orientation polarization was  $P_o = P_{2\infty} - P_i$ . From the  $\mu_s$  values determined from the  $P_o$  values in each of the solvent,  $\mu_s$  vs  $\epsilon_s$  plots were made wherein  $\mu_s \rightarrow \mu_g$  as  $\epsilon_s \rightarrow 0$ . The ratio  $\mu_s/\mu_g$  gives the  $g$  value. Excluding non-polar solvents like  $C_6H_6$  and  $CCl_4$ , the  $g$  value for the polarizable dipole placed in a continuous polar medium of permittivity  $\epsilon_s$  is given by Onsager's model as,

$$g = \frac{3\epsilon_s(n_2^2 + 2)}{(n_2^2 + 2\epsilon_s)(\epsilon_s + 2)} \quad (1)$$

However, the  $g$  values from equation (1) and the

Table 1 Correlation ( $g$ ) and form factor ( $F$ ) values of HsTs at 25°C

Solvent	I			II			III			IV			V			VI		
	$g$	$g_0$	$F$	$g$	$g_0$	$F$	$g$	$g_0$	$F$	$g$	$g_0$	$F$	$g$	$g_0$	$F$	$g$	$g_0$	$F$
<i>n</i> -hexane	1.05	1.07	0.706	1.03	1.04	0.611	0.95	0.95	0.561	1.03	1.04	0.555	1.01	1.02	0.531	1.01	1.02	0.527
CCl <sub>4</sub>	1.06	1.06	0.707	1.04	1.06	0.600	0.96	0.97	0.565	1.04	1.05	0.541	1.02	1.04	0.530	1.02	1.03	0.525
C <sub>6</sub> H <sub>6</sub>	1.07	1.08	0.705	1.08	1.07	0.615	0.97	0.98	0.562	1.05	1.04	0.545	1.04	1.05	0.535	1.03	1.04	0.528
CHCl <sub>3</sub>	1.17	1.15	0.708	1.17	1.15	0.622	0.99	0.98	0.610	1.11	1.10	0.557	1.08	1.07	0.541	1.05	1.06	0.531
<i>n</i> -BuCl	1.23	1.24	0.810	1.26	1.25	0.633	1.03	1.05	0.625	1.17	1.18	0.562	1.13	1.12	0.546	1.08	1.07	0.538
<i>n</i> -BuOH	1.64	1.64	0.815	1.68	1.67	0.637	1.20	1.21	0.636	1.50	1.51	0.568	1.33	1.35	0.551	1.22	1.21	0.541
Acetone	1.73	1.75	0.822	1.80	1.79	0.642	1.24	1.25	0.638	1.60	1.62	0.620	1.39	1.38	0.553	1.24	1.23	0.546
EtOH	1.87	1.86	0.830	1.94	1.95	0.651	1.30	1.31	0.642	1.70	1.71	0.633	1.45	1.46	0.558	1.30	1.29	0.550
MeOH	2.01	2.00	0.841	2.02	2.01	0.662	1.35	1.35	0.650	1.80	1.79	0.645	1.50	1.49	0.564	1.33	1.32	0.557

$g_0$  values refer those from Onsager's theory.

( $\mu_s/\mu_g$ ) method given in table 1 seem comparable. It is observed that for all compounds I–VI a positive solvent effect is seen as  $\mu_s > \mu_g$ .

From the existing theories of solvent effect<sup>7,8</sup> a positive solvent effect can be attributed to a molecular dipole directed along the minor axis of an ellipsoidal molecule. In the case of a HsT molecule (figure 1) the induced moment due to polarization of the  $n$ -electron cloud by the solvent dipoles should lie along the minor molecular axis, causing an increase in the resultant dipole moment ( $\mu_s$ ) of the molecule compared to  $\mu_g$ . Apart from this induced polarization contribution, even orientation polarization contribution could be envisaged for HsT type molecule where relative proportions of chair and boat conformers in solution determine the resultant  $\mu_s$ . Since the boat conformer (figure 1) has a lower  $\mu$

value (because the lone pairs do not lie on the same direction) if the solvent polarity ( $\epsilon_s$ ) increases the proportions of chair conformer in the solution, an increase in  $P_0$  and thus an increase in  $\mu_s$ , could be seen. Assuming the HsT molecules to be ellipsoids, the form factor  $F$  values<sup>9,10</sup> which are directly related to the ratio of the semi-major and minor axes of the ellipse could be evaluated using the Ross and Sack relationships

$$g = \frac{\mu_s}{\mu_g} = \frac{3\epsilon_s[1 - (n_2^2 - 1)F]}{(\epsilon_s + 2)[\epsilon_s + (n_2^2 - \epsilon_s)F]}, \quad (2)$$

and

$$g - 1 = \frac{\Delta\mu}{\mu_g} = \frac{(\epsilon_s - 1)[(\epsilon_s + 2n_2^2)F - \epsilon_s]}{(\epsilon_s + 2)[\epsilon_s + (n_2^2 - \epsilon_s)F]}. \quad (3)$$

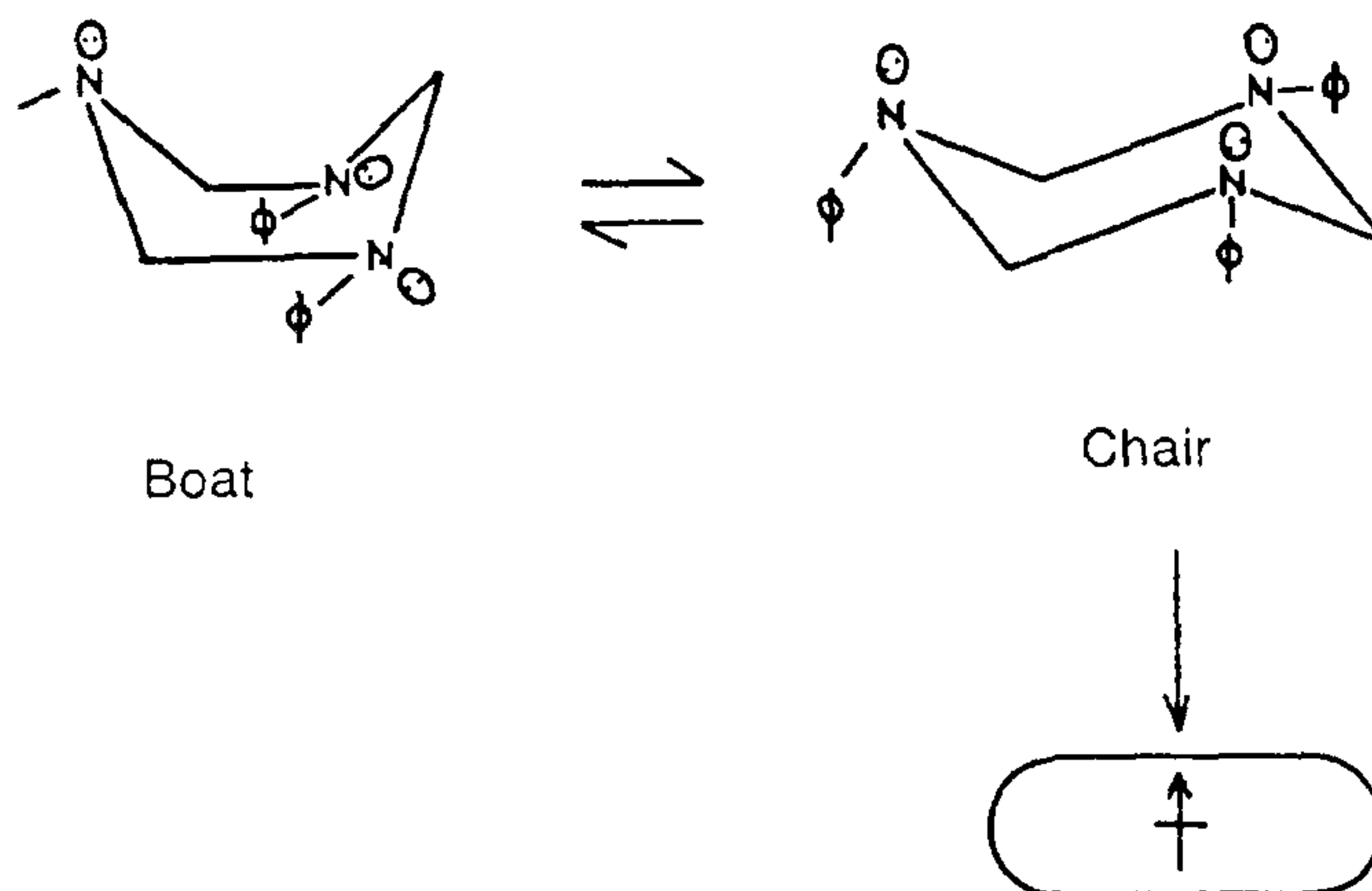


Figure 1. Molecular orientations of HsT.

Since equations (2) and (3) have been derived based on the Onsager's model,  $F$  values of the solutes I–VI were determined using the  $g$  values obtained from (1). The  $F$  values (table 1) seem to lie in the range reported for small ellipsoidal molecules.

### Linear dependences

Many authors have attempted to express solvent effects in terms of anisotropy of the solute molecular polarizability<sup>11,12</sup>. The experimental evidence supports an equation of the form  $(g-1) = A(\epsilon_s - 1)/C$

where  $C$  is either a constant or slightly dependent on  $\epsilon_s$  and  $A$  depends on the shape of the molecule and the position of the dipole within it. For a dipole placed symmetrically at the centre of the molecule with the major axis perpendicular to the dipole axis, the slope ( $A/C$ ) has a positive value, confirming a positive solvent effect. Since  $g = \mu_s/\mu_o$ , and the resultant dipole moment of the HsT molecule depends on the +I and -I effect of the *para*-phenyl substituents,  $g$  should exhibit a linear dependence on the Hammett substituent ( $\sigma_p$ ) values. Figures 2a and 2b exhibit both the  $g$  effects.

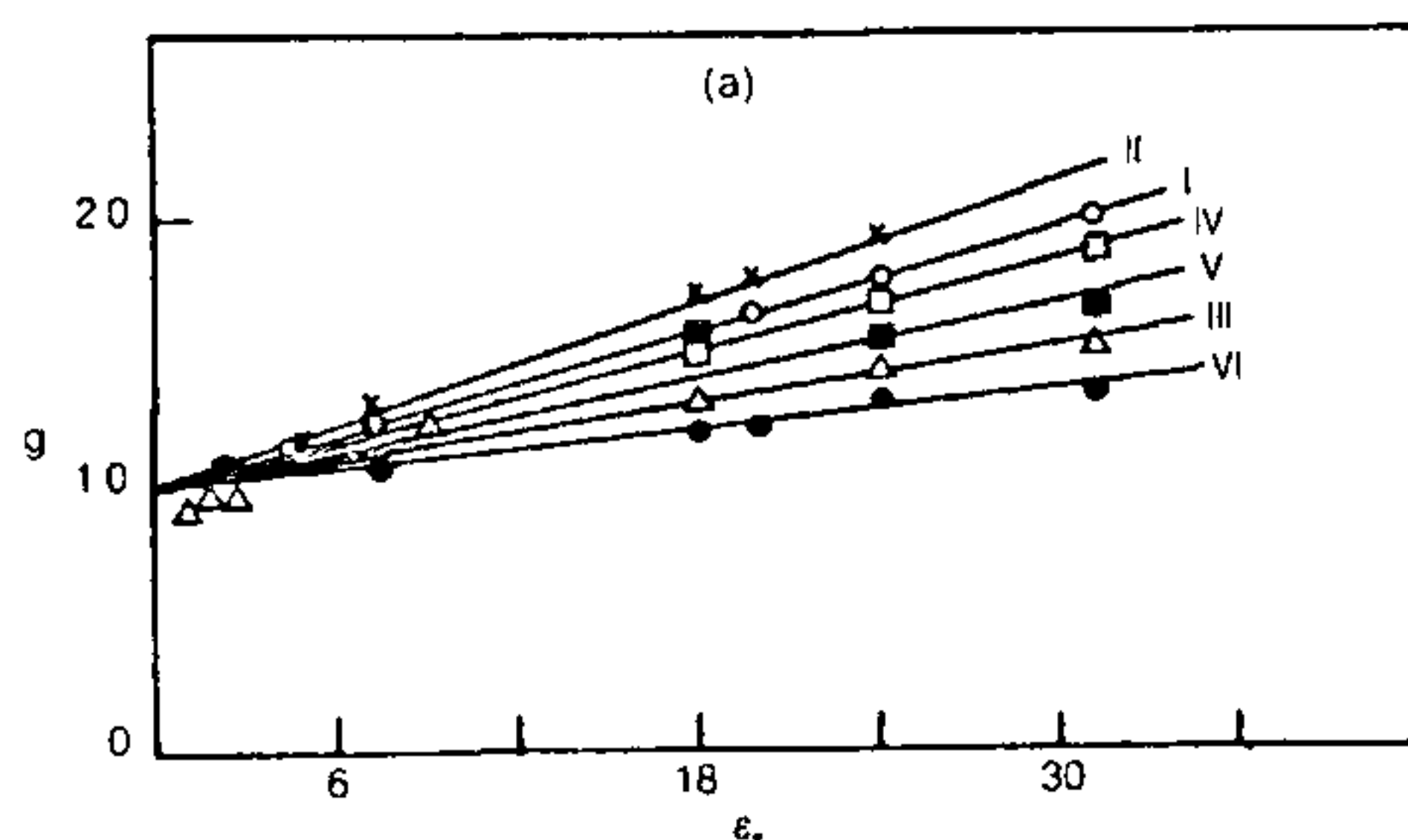


Figure 2a.  $g$  vs  $\epsilon_s$  plots I–VI HsTs.

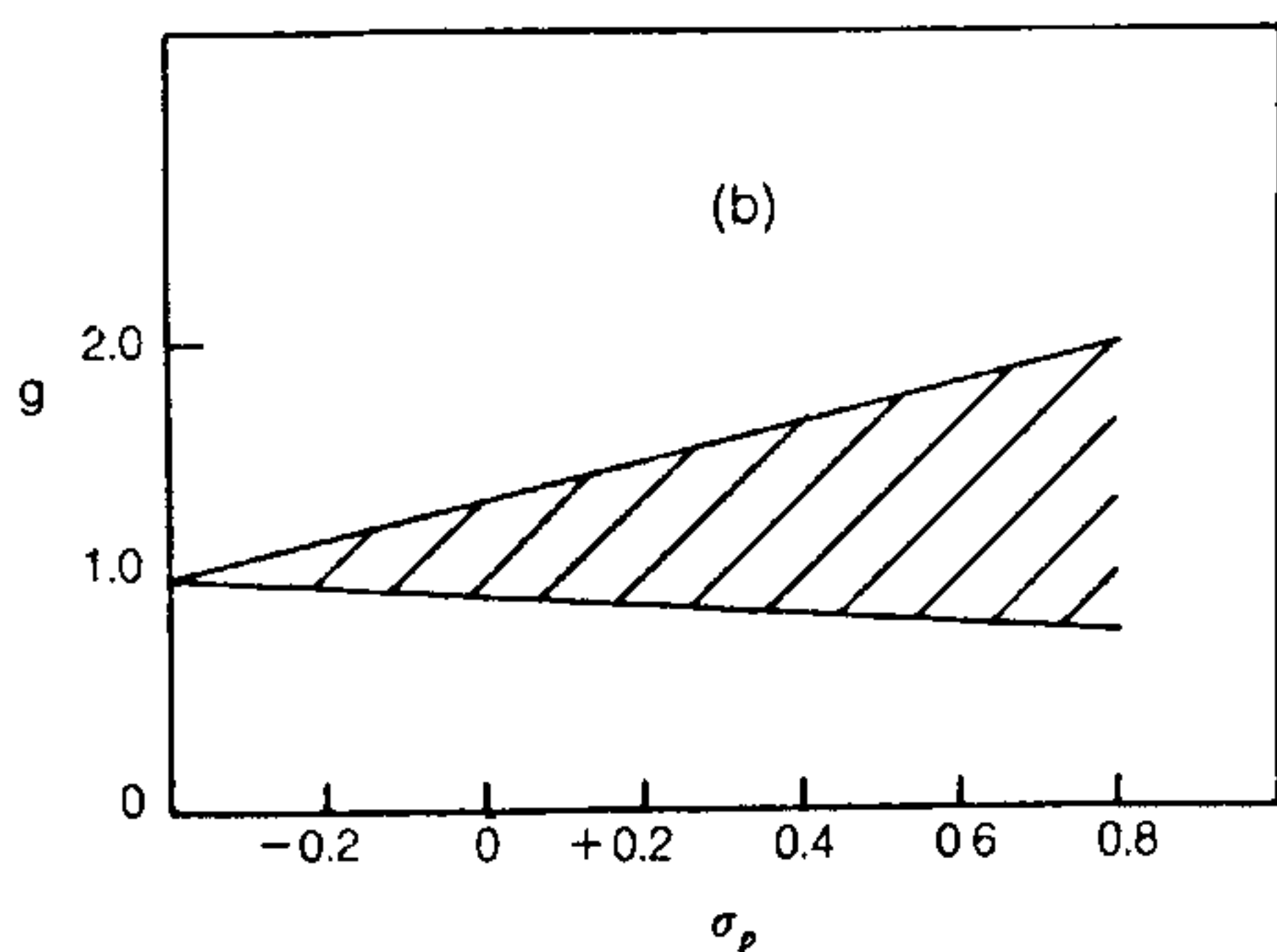


Figure 2b. Region  $g$  variation on  $\sigma_p$  for I–VI in 9 solvents.

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