

MOLAR POLARIZATIONS AND PERMANENT ELECTRIC MOMENT OF SOME HEXAHYDRO-s-TRIAZINES

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ABSTRACT

Dipole moments of six derivatives of 1,3,5-triphenylhexahydro-s-triazines are determined from the molar polarisation data of dilute solutions adopting Guggenheim's method. It is found that the dipole moment decreases with $+I$ substituents and increases with $-I$ substituents in the p -position of the phenyl ring.

INTRODUCTION

HEXAHYDRO-S-TRIAZINES are a class of compounds comprising both substituted and non-substituted saturated 1,3,5-triazacyclohexane ring systems¹. Structurally they constitute a cyclohexane ring with alternating carbon and nitrogen atoms. From figure 1, which is the structure of 1,3,5-triphenylhexahydro-s-triazine (I), it is clear that similar to cyclohexane ring, compound I can exist in both chair and boat conformations. Also, depending on the alignment of the lone pairs on the nitrogen atoms, compound I seems to possess a resultant electric dipole moment if stereochemical isomerism is present. Hence, studies on the evaluation of permanent dipole moments of a series of hexahydro-s-triazines would prove vital regarding the stereochemical aspects of these compounds. A survey of literature shows that studies on the dielectric behaviours and molar polarization and

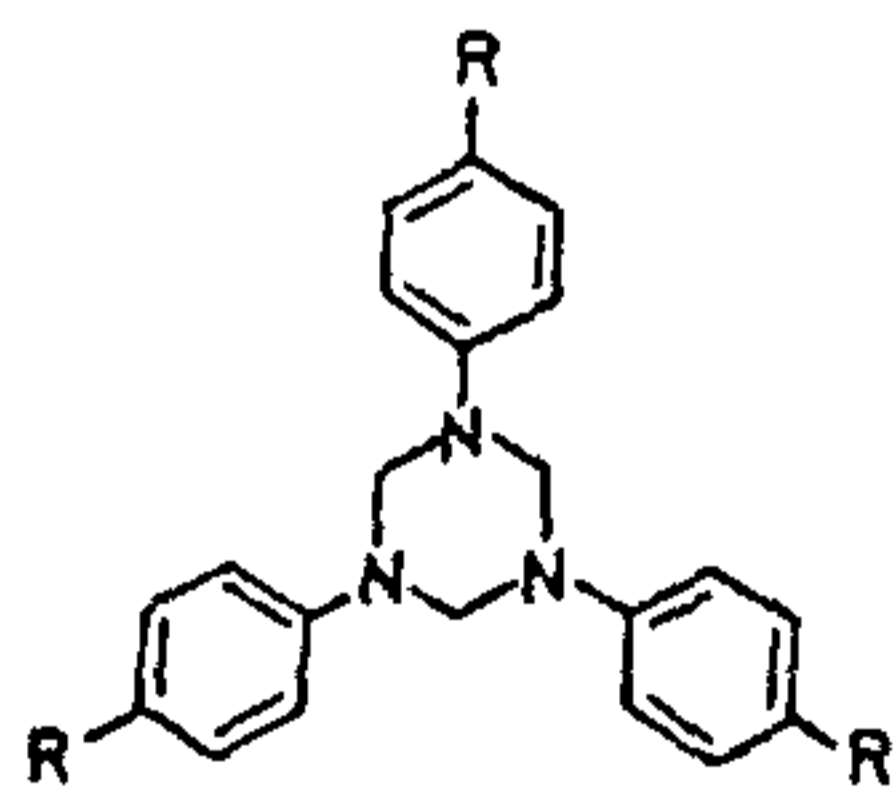
dipole moment determinations on hexahydro-s-triazines have not been carried out so far. In the present investigation molar polarization measurements and evaluation of permanent electric moments of six phenyl substituted derivatives of hexahydro-s-triazines have been undertaken. Compounds studied are: 1,3,5[-triphenyl; -tri-4-methylphenyl; -tri-4-chlorophenyl; -tri-4-methoxyphenyl; -tri-4-ethoxyphenyl; and -tri-4-nitrophenyl] hexahydro-s-triazines and are designated as compounds I, II, III, IV, V and VI respectively. Guggenheims' method² has been used to evaluate the dipole moments from the molar polarizations of dilute solutions of compounds I to VI in nonpolar solvents like benzene and carbon tetrachloride at 25°C.

EXPERIMENTAL

Spectrograde E. Merck samples of benzene $n_D^{25} = 1.5010$ and carbon tetrachloride $n_D^{25} = 1.4630$ are used. Compounds I-VI are prepared and recrystallized as mentioned elsewhere¹. The investigated concentration range was $x_2 = 0.02-0.15$ for every system. Dielectric constant measurements were carried out on a PICO-DK meter based on resonance principle at a frequency of 7 MHz, stabilized by a piezoelectric quartz crystal. Effective capacity of the cell used was 2 pF. Density measurements were performed with a pycnometer of volume 10 cc. Temperature was kept constant at 25° using an ultrathermostat fitted with external circulation. Refractive indices are determined on an Abbe's refractometer.

RESULTS AND DISCUSSION

The experimental values of dielectric constants, densities and molar volumes of solutions at various concentrations are presented in tables 1 and 2.



$R = H, CH_3-, Cl-, H_3CO-, H_5C_2O-, NO_2$

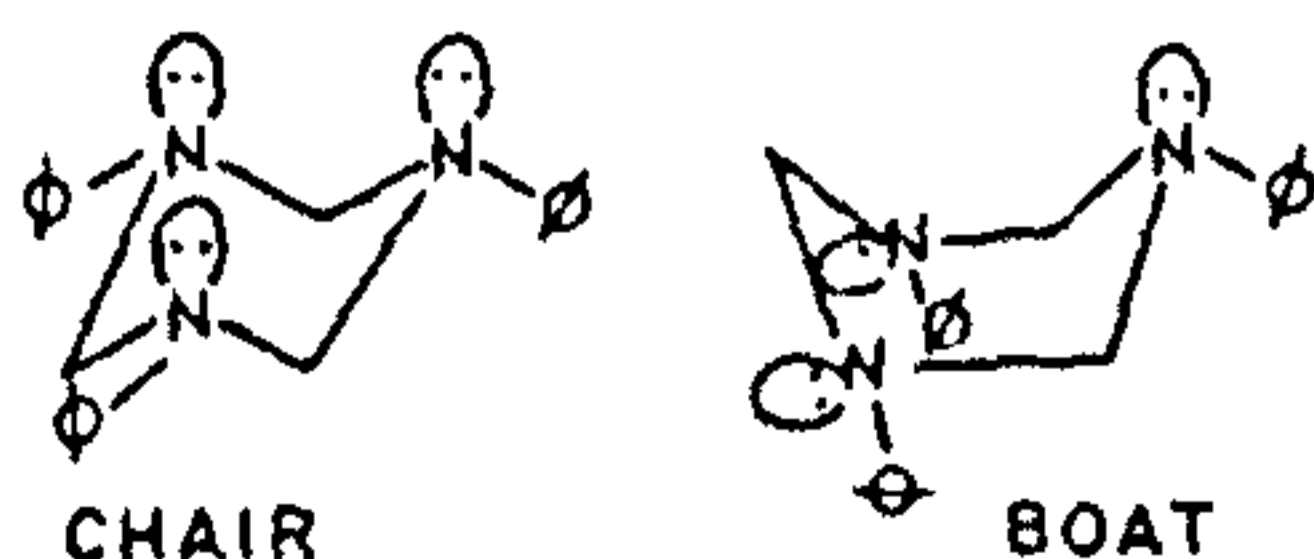


Figure 1. Hexahydro-s-triazine structure.

Table 1 Dielectric constant, density and molar polarization values in benzene and CCl₄ at 25°C

x_2	in C ₆ H ₆				in CCl ₄			
	$\epsilon_{1,2}$	$d_{1,2}$	$P_{1,2}$	P_2	$\epsilon_{1,2}$	$d_{1,2}$	$P_{1,2}$	P_2
Compound I								
0.02	2.33	0.887	28.65	119.9	2.24	1.561	29.47	116.5
0.05	2.42	0.899	32.11	133.2	2.33	1.440	34.57	165.2
0.09	2.53	0.915	36.67	136.6	2.46	1.291	42.76	195.1
0.12	2.61	0.927	40.10	137.7	2.56	1.172	50.68	219.3
0.15	2.69	0.938	43.62	139.0	2.66	1.063	59.87	242.2
Compound II								
0.02	2.34	0.880	29.32	153.3	2.23	1.529	30.24	155.0
0.05	2.42	0.890	33.19	154.8	2.31	1.351	36.96	213.0
0.09	2.53	0.903	38.57	157.7	2.42	1.135	42.53	264.2
0.12	2.61	0.910	42.78	160.0	2.51	0.962	48.98	315.3
0.15	2.69	0.920	46.94	161.1	2.59	0.793	80.88	382.3
Compound III								
0.02	2.32	0.881	29.41	160.2	2.17	1.791	25.02	105.9
0.05	2.38	0.884	33.87	168.4	2.18	1.235	38.25	238.8
0.09	2.44	0.888	39.68	170.0	2.19	0.917	55.04	331.6
0.12	2.51	0.892	44.61	175.3	2.195	0.678	78.09	447.7
0.15	2.57	0.895	49.55	178.5	2.20	0.440	125.92	682.5
Compound IV								
0.02	2.33	0.881	29.48	161.3	2.22	1.512	30.41	163.5
0.05	2.42	0.883	34.25	175.9	2.29	1.332	37.60	225.8
0.09	2.52	0.887	40.73	181.7	2.39	1.092	51.20	288.9
0.12	2.61	0.890	46.01	186.9	2.46	0.911	66.23	348.8
0.15	2.69	0.892	51.32	190.3	2.53	0.731	88.55	433.4
Compound V								
0.02	2.32	0.882	29.61	167.8	2.21	1.507	29.27	106.5
0.05	2.37	0.883	34.24	175.8	2.28	1.319	38.24	238.6
0.09	2.44	0.888	40.66	180.9	2.37	1.069	52.90	307.8
0.12	2.50	0.890	45.80	185.2	2.43	0.882	69.23	373.8
0.15	2.55	0.893	50.93	187.7	2.50	0.694	95.08	476.8
Compound VI								
0.02	2.29	0.880	29.12	160.4	2.18	1.487	30.36	161.0
0.05	2.30	0.881	32.97	155.4	2.19	1.271	37.72	228.2
0.09	2.30	0.883	38.17	153.2	2.21	0.981	52.92	307.9
0.12	2.31	0.884	42.17	154.9	2.22	0.764	71.72	394.6
0.15	2.31	0.885	45.95	154.5	2.24	0.548	105.88	548.9

Values of $P_{1,2}$ and P_2 are calculated using Debye's expressions³

$$P_{1,2} = \frac{\epsilon_{1,2} - 1}{\epsilon_{1,2} + 2} \cdot \frac{M_{1,2}}{d_{1,2}} = x_1 P_1 + x_2 P_2 \quad (1)$$

and,

$$P_2 = \frac{P_{1,2} - x_1 P_1}{x_2} \quad (2)$$

where P_1 , P_2 and $P_{1,2}$ are the molar polarizations of solvent, solute and solution respectively, $\epsilon_{1,2}$ and $d_{1,2}$

are the dielectric constant and density of the solution and $M_{1,2} = x_1 M_1 + x_2 M_2$ (where x and M denote the molefraction and molecular weight respectively). Indices 1,2 and 1,2 represent solvent, solute and solution respectively. The values of $P_{2(\infty)}$ are obtained from the extrapolation of the plots of P_2 versus x_2 as x_2 tends to zero.

As the dielectric constants and densities vary linearly with molefraction in the investigated concentration range, $P_{2(\infty)}$ values were also determined adopting Hedestrand's method^{4,5}. From table 2, it is seen that the $P_{2(\infty)}$ values determined by the two methods are seen to be in good agreement, $P_{2(\infty)}$ value denotes total polarization of the molecule

Table 2 Data on molar polarizations and dipole moments of hexahydro-s-triazine at 25°C

Compound		$P_{2(\infty)}$ (cc)			P_o cc	μ Debye
		C_6H_6	CCl_4	Hedestrand's method		
I	1,3,5-triphenyl- hexahydro-s-triazine	129.0	122.0	125.0	27.6	1.16
II	1,3,5-tri-(4-methyl)- phenyl-	149.5	146.0	147.0	18.5	0.98
III	1,3,5-tri-(4-chloro)- phenyl-	156.0	153.2	157.2	99.1	2.20
IV	1,3,5-tri-(4-methoxy)- phenyl-	160.5	160.2	165.2	46.1	1.50
V	1,3,5-tri-(4-ethoxy)- phenyl-	150.0	155.8	158.0	74.0	1.95
VI	1,3,5-tri-(4-nitro)- phenyl-	140.0	140.0	141.8	128.0	2.50

which is the sum of orientation polarization P_o and induced polarization P_i . P_i is the sum of electronic polarization P_e and atomic polarization P_a . $P_e = R_{M_{2(\infty)}}$ and $P_a \approx 0.15 R_{M_{2(\infty)}}$. The molar refractivity $R_{M_{2(\infty)}}$ of solutes is determined from the extrapolation of the plots of $R_{1,2} = f(x_2)$ as x_2 tends to zero.

The values of permanent electric moments of the six phenyl substituted hexahydro-s-triazines are listed in table 2. The dipole moment values clearly support the idea of the existence of stereochemical isomerism in these compounds. On comparing the permanent dipole moment values of individual compounds from I to VI, it is seen that if the para-substituent in the phenyl ring has a positive inductive effect (+I) the d.m. value (μ) decreases and if it has a negative inductive effect (-I) the d.m. value increases. The reason may be laid as follows. The distortion of the chair or boat conformation may occur due to the lone pair-lone pair repulsion which is enhanced in case of +I effect substituents. Also, due to the electron withdrawal of the -I effect

substituents, the repulsion between the lone pairs diminishes and the probability of a proper alignment of the lone pairs along the same direction would be greater. This effect leads to a comparative increase in the dipole moment for compounds with -I effect phenyl ring substituents.

30 August 1986; Revised 5 November 1986

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ERRATUM

The date of receipt of the following article was not mentioned by oversight:

C. N. R. RAO and P. GANGULY

Curr. Sci., 1987, 56, 47.

Date of receipt: 2 February 1987.