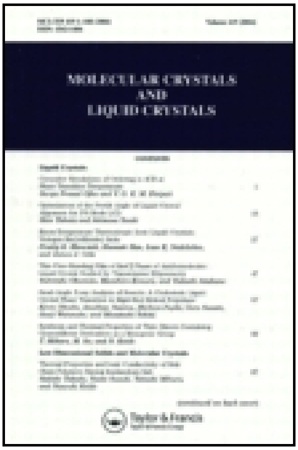

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Study on Molecular Polarizabilities of Cyclohexane Derivatives

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Study on Molecular Polarizabilities of Cyclohexane Derivatives

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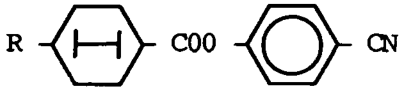
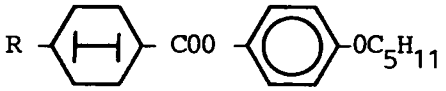
The refractive indices and densities have been measured as a function of temperature for trans-4-alkylcyclohexyl 4′-n-pentyloxyphenylester and trans-4-alkylcyclohexyl 4′-cyanophenylester in the liquid crystalline and liquid phases. The molecular polarizabilities have been evaluated by Vuks' formula. The polarizabilities obtained are compared with those estimated from bond polarizability calculations for the molecules. The relative nematic stabilities of the cyclohexane derivatives are discussed in terms of the molecular parameters measured.

INTRODUCTION

The molecular polarizabilities and their anisotropy are important values for characterizing liquid crystalline substances since they play a significant role in the intermolecular interaction. Molecular polarizabilities, though impossible to measure directly, can be calculated from the temperature dependence of refractive indices and densities on the bases of Vuks' model[1] in which the local field is taken to be isotropic. In the series of cyclohexane derivatives, especially the 4-cyanophenyl and 4-n-alkyloxy phenyl ester are of interest in the comparatively high clearing temperature in spite of low optical anisotropy and low viscosity. In this paper, we present the results of refractive index, density and the molecular polarizabilities for the two kinds of series of the cyclohexane derivatives. Comparison of calculated and experimental values of the polarizabilities provides information of conjugated region of molecular structure. Moreover, the stabilities of cyclohexane derivatives are discussed in terms of intermolecular forces due to a mean field theory,[2,3,4] and extended one[5,6] using these experimental data.

TABLE I

The abbreviations C and P stand for compounds with cyano group and pentyloxy, and the numbers refer to the numbers of carbon atoms in alkyl chain

Name and Formula	R	T_{K-N}(°C)		T_{N-I}(°C)	Abbreviation
	C_3H_7	52.0	-	70.0	C-3
	C_4H_9	54.7	-	69.9	C-4
	C_5H_{11}	47.4	-	79.5	C-5
trans-4-alkyl cyclohexyl 4'-cyanophenyl ester.					
	C_3H_7	37.3	-	66.2	P-3
	C_4H_9	29.5	-	66.5	P-4
	C_5H_{11}	34.1	-	75.9	P-5
trans-4-alkyl cyclohexyl 4'-n-pentyloxy phenyl ester.					

EXPERIMENTAL

The structural formula and the nematic-isotropic transition temperatures of trans-4-alkylcyclohexyl 4'-pentyloxyphenylester and trans-4-alkylcyclohexyl 4'-cyanophenylester used in this study are shown in Table I. The liquid crystals were obtained from MERCK & Co, and were used without further purification. The refractive indices n_o and n_e for ordinary and extraordinary ray were measured with an Abbe refractometer attached to a thermostated circulating water bath. The glass prism of the refractometer was rubbed with a lens paper along the length of the prism several times to align the molecules of the liquid crystals on the prism surface. An analyzer was set on the eyepiece of an Abbe refractometer to make the shadow edge clear. The transition temperatures were determined by a polarizing microscope with a Mettler heating stage in which temperature could be controlled electrically to an accuracy of ±0.1°C. The density was determined as a function of temperature in a capillary dilatometer of nearly 0.2 cm^3 in volume with an approximate error of ±0.0005g/cm^3.[3] The dilatometer was held in a thermostat whose temperature could be controlled to ±0.1°C.

RESULTS AND DISCUSSION

The refractive indices of the ordinary n_o and of the extraordinary ray n_e and densities of 4-trans-4-alkylcyclohexyl 4'-n-pentyloxyphenylester(P-series) and 4-trans-4-alkylcyclohexyl 4'-cyanophenylester(C-series) are presented in Tables II and III as a function of temperature. The temperature dependences of the refractive indices for two kinds of materials are shown in Figure 1. The values ($\Delta n < 0.1$) of birefringence for P-series are smaller than those ($\Delta n \sim 0.12$) for C-series. In Vuks' model,[1] it is assumed that the internal field is isotropic even in an anisotropic crystal. This approach leads to the following equation:

$$\frac{n_{e,o}^2 - 1}{\overline{n}^2 + 2} = \frac{4\pi N \alpha_{e,o}}{3}$$

where N is the number of molecules per unit volume, $\overline{n}^2 = (n_e^2 + 2n_o^2)/3$, and the effective polarizabilities α_e and α_o correspond to the electric vector parallel and perpendicular to the optic axis, respectively. The molecular polarizabilities ($\alpha_{\parallel}$, $\alpha_{\perp}$) are calculated from α_e

TABLE II

Densities and refractive indices, λ = 589.3 nm, in the nematic and isotropic phases of trans-4-alkylcyclohexyl 4′-n-pentyloxyphenylester

P-5				P-4				P-3			
Temp °C	Density g/cm^3	n_e	n_o	Temp °C	Density g/cm^3	n_e	n_o	Temp °C	Density g/cm^3	n_e	n_o
35.0	0.9744	1.5522	1.4710	30.0	0.9984	1.5521	1.4749	38.5	1.0140	1.5483	1.4725
36.5	0.9727	1.5508	1.4700	33.0	0.9959	1.5498	1.4742	41.3	1.0117	1.5459	1.4719
38.3	0.9707	1.5494	1.4700	35.9	0.9934	1.5477	1.4734	43.6	1.0098	1.5440	1.4713
40.7	0.9681	1.5476	1.4697	39.0	0.9908	1.5454	1.4736	46.0	1.0079	1.5418	1.4713
45.7	0.9627	1.5438	1.4688	42.0	0.9882	1.5429	1.4721	50.7	1.0042	1.5373	1.4702
50.0	0.9581	1.5403	1.4680	45.0	0.9857	1.5403	1.4723	53.9	1.0016	1.5341	1.4698
53.8	0.9540	1.5369	1.4670	47.7	0.9835	1.5377	1.4710	63.3	0.9943	1.5178	1.4705
56.0	0.9517	1.5350	1.4666	51.6	0.9821	1.5338	1.4703	63.9	0.9938	1.5164	1.4710
58.0	0.9496	1.5329	1.4662	55.1	0.9773	1.5298	1.4702	64.3	0.9935	1.5153	1.4712
60.8	0.9467	1.5300	1.4659	56.8	0.9759	1.5276	1.4700	64.8	0.9931	1.5133	1.4720
62.9	0.9445	1.5275	1.4657	58.5	0.9745	1.5254	1.4700	65.0	0.9929	1.5115	1.4725
67.3	0.9399	1.5217	1.4654	60.7	0.9727	1.5212	1.4702	66.2	0.9870	1.4842	
70.0	0.9371	1.5169	1.4660	63.1	0.9708	1.5154	1.4712				
71.0	0.9361	1.5150	1.4662	64.2	0.9699	1.5103	1.4738				
73.0	0.9341	1.5077	1.4680	66.5	0.9680	1.4840					
75.6	0.9255	1.4795									

TABLE III

Densities and refractive indices, λ = 589.3 nm, in the nematic and isotropic phases of trans-4-alkylcyclohexyl 4′-cyanophenyl ester

C-5				C-4				C-3			
Temp °C	Density g/cm^3	n_e	n_o	Temp °C	Density g/cm^3	n_e	n_o	Temp °C	Density g/cm^3	n_e	n_o
48.7	1.0116	1.5770	1.4739	55.0	1.0503	1.5658	1.4777	52.0	1.0715	1.5792	1.4775
52.3	1.0136	1.5736	1.4730	55.8	1.0496	1.5645	1.4776	53.0	1.0706	1.5780	1.4772
55.8	1.0081	1.5672	1.4722	57.4	1.0481	1.5622	1.4776	54.4	1.0693	1.5764	1.4770
61.2	1.0061	1.5645	1.4719	58.5	1.0471	1.5604	1.4776	56.0	1.0678	1.5743	1.4770
62.8	1.0048	1.5626	1.4718	60.0	1.0456	1.5580	1.4778	56.9	1.0670	1.5731	1.4770
65.2	1.0028	1.5597	1.4718	62.1	1.0437	1.5542	1.4783	58.0	1.0660	1.5717	1.4770
66.5	1.0017	1.5576	1.4718	62.9	1.0430	1.5526	1.4786	58.9	1.0652	1.5704	1.4770
70.1	0.9988	1.5526	1.4718	64.1	1.0409	1.5455	1.4800	60.9	1.0634	1.5671	1.4772
71.7	0.9974	1.5492	1.4722	66.0	1.0401	1.5423	1.4810	62.9	1.0616	1.5636	1.4774
73.5	0.9959	1.5454	1.4728	67.0	1.0392	1.5348	1.4835	64.8	1.0599	1.5597	1.4779
74.5	0.9953	1.5434	1.4728	68.9	1.0341	1.4988		68.0	1.0570	1.5487	1.4803
75.0	0.9947	1.5420	1.4733					68.6	1.0545	1.5448	1.4817
80.0	0.9855	1.4968						71.7	1.0486	1.002	

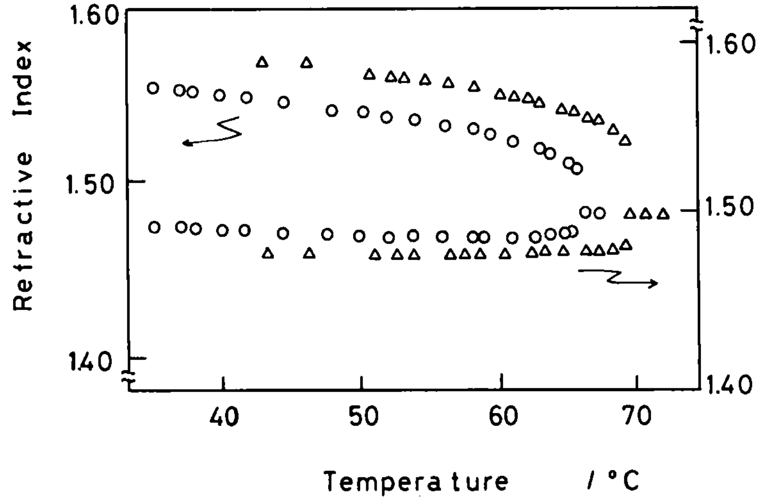


FIGURE 1 Temperature dependence of refractive indices of trans-4-propylcyclohexyl 4′-n-pentyloxy phentylester (○) and trans-4-propyl cyclohexyl 4′-cyanophenyl ester (△).

and α_o by using the Haller's extrapolation procedure,[7] in which the value of $\log(\alpha_e / \alpha_o)$ vs $\log(T_c - T)$ is assumed to be $\log(\alpha_{\|}/\alpha_{\perp})$ at $T = 0\text{K}$, where T_c is the nematic-isotropic temperature. The molecular polarizabilities for P-series and C-series are presented in Table IV. The electronic polarizabilities of the molecules were also estimated from the addition of tabulated bond polarizabilities.[8] The conjugated regions in the compounds of P- and C-series were taken as $\text{—COOC}_6\text{H}_4\text{O}$ and $\text{—COOC}_6\text{H}_4\text{CN}$, respectively. For the bonds of conjugated region, we used the values of double bond polarizabilities. The molecular axis is assumed to be along the line joining the centers of the benzene ring and cyclohexane ring on the basis of structural formula assuming that molecules have the all-trans conformation. When a bond makes an angle θ with molecular axis, the polarizability parallel to the molecular axis summed for all bonds is given by $\alpha_{\|} = \Sigma\beta_l\cos^2\theta + \Sigma\beta_t\sin^2\theta$, where β_l and β_t are bond polarizabilities parallel and transverse to the bond, respectively. The β_l of the C—C and C—H bonds of the end group is taken to that of the C—C bond and C—H bonds of the isotropic polarizabilities. An estimation of the polarizability anisotropy ($\Delta\alpha = \alpha_{\|} - \alpha_{\perp}$) is made by using $(3/2)(\alpha_{\|} - \bar{\alpha})$, taking the average polarizability $\bar{\alpha}$. The values for the molecular polarizability computed using bond polarizabilities are given in Table IV. Comparison of calculated and experimental values of the polar-

TABLE IV

The molecular polarizabilities and the average polarizability of P-series and C-series determined by extrapolation procedure using the Vuks relation and by the addition of bond polarizabilities, and substance constant **A**

Substance	Experimental values (in $10^{-24}cm^3$)			Caluculated values (in $10^{-24}cm^3$)			Substance constant (in $10^{-9}erg\cdot cm^6$)
	$\bar{\alpha}$	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\bar{\alpha}$	$\alpha_{\parallel}$	$\alpha_{\perp}$	**A**
C-3	30.13	38.41	26.00	31.34	36.55	28.78	15.52
C-4	32.44	41.04	27.58	33.18	39.32	30.11	18.50
C-5	35.20	44.66	30.44	35.03	41.79	31.64	20.58
P-3	38.16	45.31	33.53	38.85	46.86	34.34	23.97
P-4	40.62	48.65	36.60	40.69	48.65	36.60	27.30
P-5	43.76	52.94	39.17	42.55	52.23	37.71	32.93

izabilities provides a test of the additivity schemes and also yields information on the conformation of the terminal alkyl chain. The polarizability values obtained from the calculation agree well with the experimental values for P-series as shown in Figure 2. For the C-series, the calculated $\alpha_{\parallel}$ values are comparatively lower than experimental values. Therefore, the calculated $\alpha_{\perp}$ values show somewhat higher than that of experimental values as shown in Figure 3. One must be content with the electronic polarizability approximation taking into consideration the accuracy of experiment and the simple model of calculation adopted. From the relations described above, such a treatment for conjugated system is valid for the series studied.

In order to understand the stability of cyclohexane derivatives, the intermolecular interactions are necessary to consider. In the Maier-Saupe theory, only anisotropic dispersion forces are responsible for the existence of the nematic phase. The nematic to isotropic transition temperature T_c in this theory, is predicted by the $A/4.54k_bV^2$ equa-

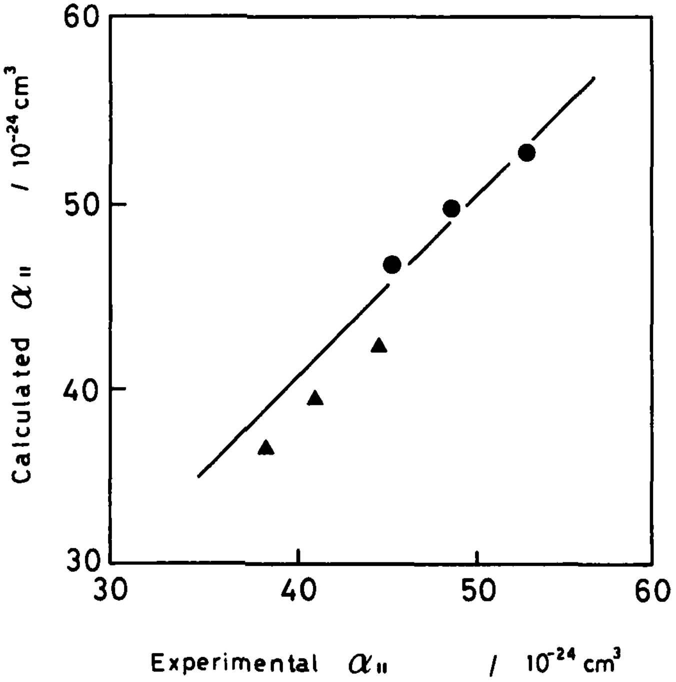


FIGURE 2 Plot of experimental $\alpha_{\parallel}$, vs calculated $\alpha_{\parallel}$ for trans-4-alkylcyclohexyl 4'-n-pentyloxy phenylester (●) and trans-4-alkyl cyclohexyl 4'-cyanophenyl ester (▲).

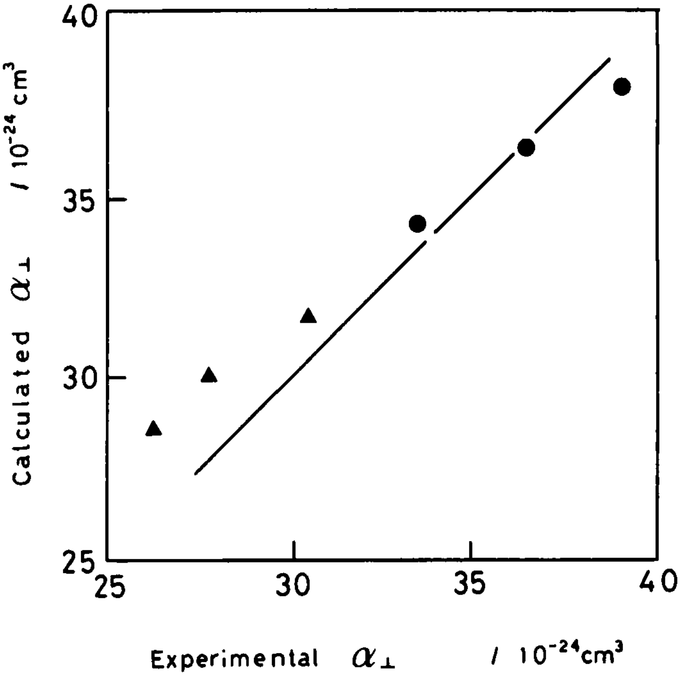


FIGURE 3 Plot of experimental $\alpha_\perp$, vs calculated $\alpha_\perp$ for trans-4-alkylcyclohexyl 4'-n-pentyloxy phenylester (●) and trans-4-alkyl cyclohexyl 4'-cyanophenyl ester (▲).

tion, where k_b is Boltzmann's constant, A is the substance constant and relates to the strength of dispersion forces, V is the molar volume of nematic phase at the clearing point. The values of A calculated from V and T_c are shown in Table IV. As the mean field model of Maier and Saupe focuses on attractive dispersion interactions parameterized via the magnitude of the anisotropy of molecular polarizability, the relation between A and $(\Delta\alpha)^2$ can be expected. The proportionality of A to $(\Delta\alpha)^2$ for each of the series is shown in Figure 4. There is a good correlation between the substance constant A and observed $(\Delta\alpha)^2$ values. The magnitude of A depends on the end alkyl chain length due to the anisotropy of polarizability. As shown in Figure 4, the value of A approaches zero as $(\Delta\alpha)^2$ comes close to zero. The lines for C-series and P-series have different slopes.These slopes are explained from the difference in the ionization energy between two series. This is ascribed to the different substituent effects of Electron-repelling group ($-OC_5H_{11}$) and great Electron-withdrawing group ($-CN$) on the basis of molecular structure.

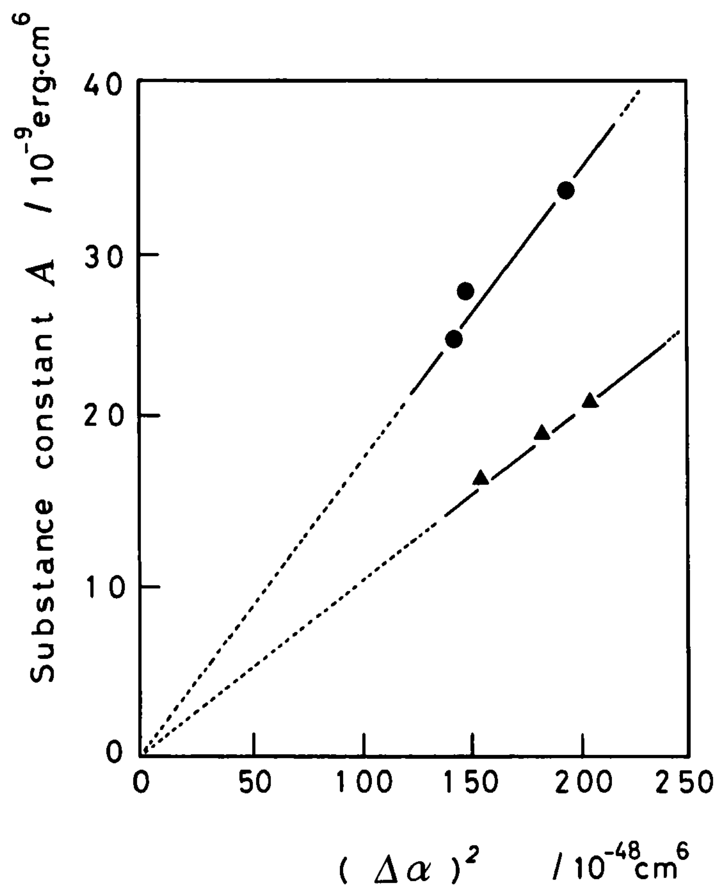


FIGURE 4 Plot of the substance constant A, vs anisotropy of molecular polarizability $(\Delta\alpha)^2$ for trans-4-alkyl-cyclohexyl 4'-n-pentyloxy phenylester (●) and trans-4-alkyl cyclohexyl 4'-cyanophenyl ester (▲).

As is different from Maier-Saupe model, there is a rigid-body repulsion model focused on anisotropic repulsive interactions where the shape anisotropy of the nematogen in terms of its axial ratio is the dominant parameter.[9,10] In general, we must consider the role of the repulsive interactions in stabilizing of the cyclohexane derivatives. The mean field model has been refined and extended by de Jeu[5] and Kimura,[6] and the "hybrid" model combining both attractive and repulsive interactions has been considered. The substance constant A according to Kimura's formulation is given as

$$A = k_b T_c V^2 \{4.54 - (5\pi/32)\Delta\nu \cdot n\}$$

where $(5\pi/32)\Delta\nu\cdot n$ is the term of the molecular geometry dependency which is due to the rigid-body repulsions, $\Delta\nu$ is given by $2D^2(1-D/L)^2$, L the length, D the breadth of molecules, $n = N/V$ is the concentration of molecules. Using the following relation $\mathbf{A} = (I/4)(\Delta\alpha)^2$ by the simple Drude model, where I is ionization energy of molecule, we can obtain the following equation

$$^{I}/_{4}(\Delta\alpha)^2 = k_b T_c V^2 \{4.54 - (5\pi/32)\Delta\nu n\}$$

In Figure 5, $(\Delta\alpha)^2$ is plotted against $T_c V^2$ for P- and C- homologous series, and these plots are compared with the reported value for p,p'-di-n-alkoxy-azoxybenzenes (PAA-series)[11] for example. Two types

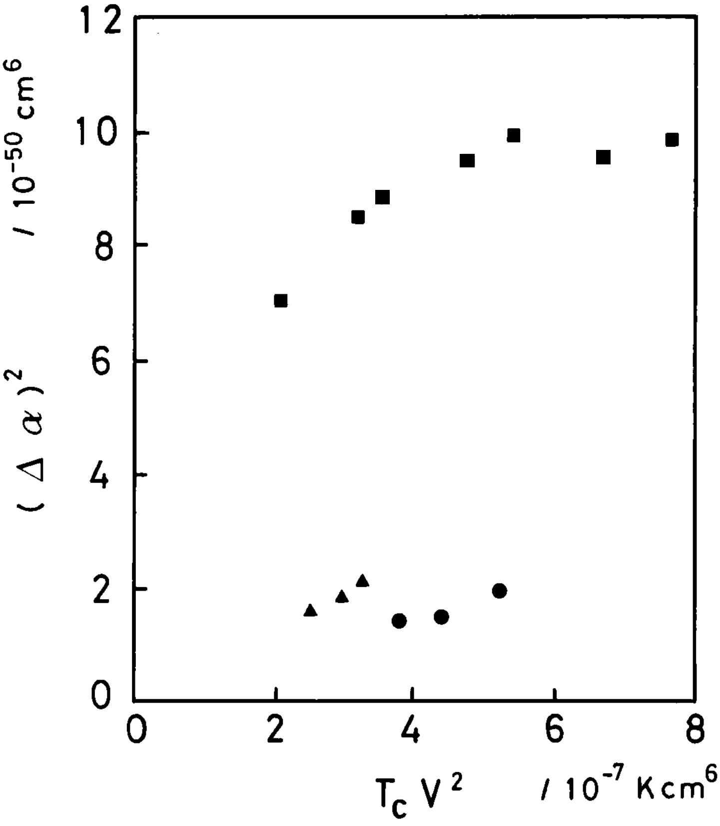


FIGURE 5 Plot of $(\Delta\alpha)^2$, vs T_cV^2 for trans-4-alkyl cyclohexyl 4'-n-pentyloxy phenylester (●), trans-4-alkyl cyclohexyl 4'-cyanophenyl ester (▲), and p,p'-di-n-alkoxy-azoxybenzenes (■).

of pattern have been observed in Figure 5; (i) $(\Delta\alpha)^2$ is linearly related to the T_cV^2 for P and C series. (ii) $(\Delta\alpha)^2$ rises simply with increasing the T_cV^2 within the short range of smaller number of alkyl chain, then $(\Delta\alpha)^2$ becomes constant for PAA series. This result can be accounted for by the above equation. If the variation in length/breadth ratio of the molecule is negligible small and ionization potentials can be regarded as being constant for the homologous series, then $(\Delta\alpha)^2$ should proportional to T_cV^2 for an homologue. In other case the molecular length/breadth ratio becomes marked larger with the increase of alkyl chain length and the repulsive interaction will become effective, the appreciable deviation may arise from the linear correlations between $(\Delta\alpha)^2$ and T_cV^2. This is expected to be the case for PAA-series. Since P- and C-series used in this study are the cyclohexane derivatives and the flexible molecules, it seems to be necessary to take the effect of flexibility into consideration in the above equation. Due to the molecular flexibility, the flexibility in these compounds reduce the rigid-body repulsion of the perfect rigidity. In conclusion, these results indicate that the rigid-body repulsive interactions make a minor contribution to the stability of the compounds with the shorter alkyl chain of the cyclohexane derivatives.

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