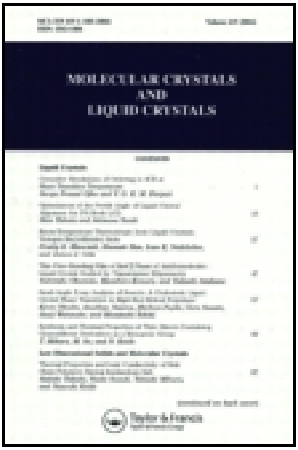

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Some Physical Properties of Mesogenic 4-(trans-4′-n-Alkylcyclohexyl) Isothiocyanatobenzenes†

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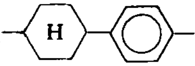
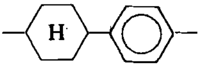
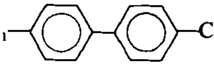
Temperature dependences of density, refractive indices, and dielectric constants have been measured for mesogenic compounds of C_kH_{2k+1}—NCS, as well as for some of their cyano-analogues: C_kH_{2k+1}—CN and C_kH_{2k+1}CN. The effects of substituting a phenyl ring by a cyclohexyl ring, as well as of a —CN group by an —NCS group have been analyzed. The results lead to the following conclusions: (i) the above exchange of rings leads to mesogens the long molecular axes of which do not coincide with the axes of the terminal groups, —CN or —NCS; (ii) antiparallel correlation of molecular dipoles found for cyano-mesogens does not occur in the case of isothiocyanato-mesogens.

INTRODUCTION

The aim of this paper is to present and discuss some physical properties of recently synthesized compounds belonging to the homologous series of 4-(*trans*-4′-n-alkylcyclohexyl)isothiocyanatobenzenes

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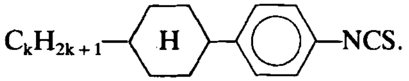
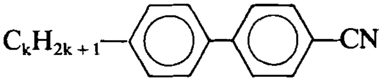
(CHBT) of general formula

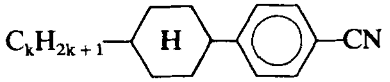


The homolologues with k = 3, 4, 5, 6, 7, 8, 9 and 10, studied by us, are nematics. Their temperature dependences have been measured for such quantities as: (i) density $\rho(T)$; (ii) refractive indices: isotropic $n_i(T)$, extraordinary $n_e(T)$ and ordinary $n_o(T)$; (iii) dielectric constants: isotropic $\epsilon_i(T)$, as well as parallel $\epsilon_{\parallel}(T)$ and perpendicular $\epsilon_{\perp}(T)$ to the director of the aligned nematic sample. This was the basis for calculating the following quantities: (i) the mean α, longitudinal α_l, and transverse α_t polarisabilities, using the well known formulae by Lorentz-Lorenz for the isotropic phase, and those by Neugebauer-Saupe-Maier[1] for the nematic phase; also the extrapolation procedure of Subramhanyam[2] was used; (ii) the effective dipole moment μ and angle β between the vector $\vec{\mu}$ and the long axis of the molecule, making use of Maier and Meier's formulae.[3] The results have been compared with analogous results for nematic 4-n-alkyl-4'-cyanobiphenyls (CB)



(k = 5, 6, 7, 8)

and 4-(*trans*-4'-n-alkylcyclohexyl)cyanobenzenes (PCH)



(k = 5, 7, 10).

This enables us to draw conclusions relating to (i) the structure of molecules in the CHBT series; (ii) the effect of substituting the —CN group by a —NCS group and of the phenyl ring by a cyclohexyl ring on the polarisability and dipole moment of molecules; (iii) the virtual association of the molecules under consideration.

EXPERIMENTAL

The refractive indices were measured by means of an appropriately prepared Abbé refractometer for $\lambda = 589$ nm. The experimental errors were of the order: $\Delta n_i = \Delta n_o = 0.0002$, and $\Delta n_e = 0.0005$. The temperature of the samples was stabilized to an accuracy of 0.3 K. Measurements have been carried out for all nematics enumerated in the Introduction.

Density was measured by means of a pycnometer. The experimental error was of the order 0.4 kg/m^3. Measurements have been carried out for three homologues in the PCH series and for two homologues (k = 3 and 6) of the CHBT series. For the remaining nematics of the latter series, their densities have been evaluated by resorting to refractive indices and the previously established linear dependence of the mean polarizability of molecules on the number of carbon atoms in the alkyl chains.[4] The error of such an evaluation does not exceed 0.4%. Densities for the CB series have been taken from the literature.[5,6]

Dielectric constants have been determined by measuring the cell capacity in the form of a condenser filled with the nematic under study. The thickness of the nematic layer was 220 μm, and the voltage used had its amplitude equal to 3 V and a frequency of 1592 Hz. In the nematic phase, the samples were aligned with a magnetic field of *ca.* 1 *T*. Nematic 5CHBT is monotropic, and we failed to supercool it for the dielectric measurements. Nematics of the CHBT series displayed a high electrical resistance (*ca.* 10^9 Ω cm). On the other hand, the compounds of the PCH series had a low resistance, e.g., in the case of 10PCH, this prevented us from obtaining reproducible results in the dielectric measurements. The results for the CHBT series (smoothed and interpolated) are collected in Table I.

DISCUSSION AND CONCLUSIONS

The mean polarisability α calculated from $n_i(T)$ and $\rho(T)$ for 6CHBT amounts to $\alpha_6 = 39.04 \pm 0.03$ Å^3. For other members of the series (k ≠ 6), α_k was calculated from the formula

$$\alpha_k = \alpha_6 + 1.87\,(k-6)\ \text{Å}^3 \qquad (1)$$

where 1.87 ± 0.01 Å^3 is the mean polarisability of the methylene group in the alkyl chains of nematogens.[4] The dependences of the longitudinal α_l and transverse α_t polarisabilities for the three series under consideration are shown in Figures 1 and 2.

A comparison of the polarisabilities α, α_l, and α_t of corresponding (the same k) members of various homologous series enabled us to evaluate changes δα, $\delta\alpha_l$ and $\delta\alpha_t$ in these quantities which are brought about by substitution of a phenyl by a cyclohexyl ring or of a —CN by an —NCS group. These changes are collected in Table II. The change in the mean polarisability caused by substitution of a phenyl by a cyclohexyl (−0.57 Å^3) ring is close to the difference[7] in the mean polarisabilities of cyclohaxane and benzene (−0.7 Å^3). Therefore, it

TABLE I

Clearing temperatures T_c, densities ρ, refractive indices (n_i, n_o, n_e) and dielectric constants (ϵ_i, $\epsilon_\perp$ $\epsilon_\parallel$) of the 4-(*trans*-4′-n-alkylcyclohexyl)isothiocyanatobenzenes

$T - T_c$	k = 3		$T_c = 313.8$ K			k = 4		$T_c = 306.3$ K		
K	ρ (g/cm^3)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$	ρ (g/cm^3)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$
10	1.018	1.5760	—	6.5	—	1.012	1.5730	—	6.7	—
5	1.021	1.5782	—	6.7	—	1.015	1.5750	—	6.8	—
3	1.022	1.5784	—	6.7	—	1.017	1.5761	—	6.8	—
2	1.023	1.5795	—	6.8	—	1.017	1.5763	—	6.8	—
−2	1.032	1.5313	1.6886	5.2	11.0	1.023	1.5354	1.6638	5.1	10.1
−3	1.033	1.5303	1.6923	5.1	11.5	1.024	1.5367	1.6690	5.0	10.5
−5	1.034	1.5288	1.6968	4.9	12.5	1.025	1.5339	1.6744	4.9	11.1
−10	1.034	1.5263	1.7010	4.5	13.5	1.029	1.5310	1.6873	4.6	12.2
−15	—	—	—	—	—	1.032	1.5302	1.6948	4.5	13.0
−20	—	—	—	—	—	1.033	1.529	1.700	4.5	13.0

$T - T_c$	k = 5		$T_c = 323.8$ K			k = 6		$T_c = 316.1$ K		
K	ρ (g/cm^3)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$	ρ (g/cm^3)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$
10	0.991	1.5601	—	—	—	0.986	1.5573	—	6.3	—
5	0.995	1.5622	—	—	—	0.989	1.5595	—	6.3	—
3	0.996	1.5631	—	—	—	0.991	1.5605	—	6.4	—
2	0.997	1.5638	—	—	—	0.991	1.5607	—	—	—
−2	1.004	1.5228	1.6552	—	—	0.997	1.5265	1.6382	4.5	9.4
−3	1.004	1.5220	1.6580	—	—	0.998	1.5248	1.6443	4.4	10.2
−5	1.006	1.5199	1.6648	—	—	1.000	1.5230	1.6502	4.4	10.5
−10	1.010	1.5168	1.6795	—	—	1.002	1.5212	1.6588	4.2	11.1
−15	—	—	—	—	—	1.007	1.5202	1.6695	4.1	11.5
−20	—	—	—	—	—	1.010	1.5194	1.6764	4.0	12.0

TABLE I (*continued*)

$T - T_c$	k = 7		T_c = 325.5 K			k = 8		T_c = 320.4 K		
K	ρ (g/cm³)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$	ρ (g/cm³)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$
10	0.973	1.5490	—	5.7	—	0.968	1.5470	—	5.2	—
5	0.976	1.5511	—	5.7	—	0.971	1.5490	—	5.2	—
3	0.977	1.5523	—	5.7	—	0.973	1.5502	—	5.3	—
2	0.978	1.5526	—	5.7	—	0.974	1.5505	—	5.3	—
−2	0.984	1.5189	1.6298	4.8	8.2	0.979	1.5195	1.6205	4.1	7.3
−3	0.985	1.5179	1.6330	4.7	8.1	0.980	1.5178	1.6264	4.0	7.7
−5	0.986	1.5150	1.6430	4.6	8.3	0.982	1.5158	1.6340	4.0	8.0
−10	0.991	1.5130	1.6530	4.6	9.7	0.985	1.5140	1.6436	3.9	8.7
−15	0.995	1.5127	1.6620	4.7	10.1	0.988	1.5125	1.6528	3.9	9.1
−20	0.998	1.5122	1.6702	4.8	10.6	—	—	—	—	—

$T - T_c$	k = 9		T_c = 325.7 K			k = 10		T_c = 323.6 K		
K	ρ (g/cm³)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$	ρ (g/cm³)	n_i, n_o	n_e	$\epsilon_{i/\perp}$	$\epsilon_\parallel$
10	—	—	—	—	—	0.954	1.5380	—	4.9	—
5	0.963	1.5434	—	5.1	—	0.957	1.5404	—	4.9	—
3	0.964	1.5443	—	5.1	—	0.958	1.5414	—	4.9	—
2	0.965	1.5448	—	5.1	—	0.958	1.5418	—	4.9	—
−2	0.971	1.5127	1.6191	4.0	7.9	0.964	1.5120	1.6060	4.1	6.7
−3	0.972	1.5112	1.6235	4.1	8.2	0.965	1.5111	1.6137	3.9	7.3
−5	0.973	1.5094	1.6301	4.1	8.6	0.967	1.5090	1.6228	3.9	7.8
−10	0.978	1.5074	1.6421	4.3	9.3	0.971	1.5068	1.6339	3.8	8.4
−15	0.982	1.5070	1.6510	—	—	0.975	1.5065	1.6420	3.8	9.0

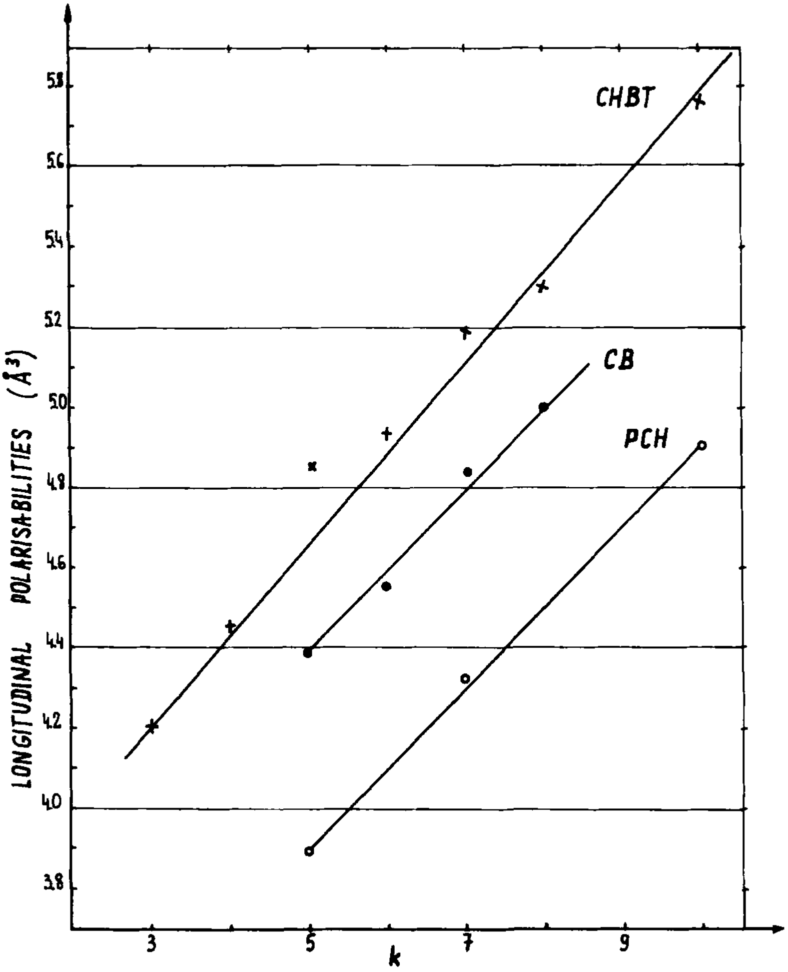


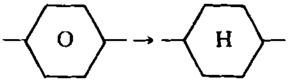
FIGURE 1 Longitudinal polarisabilities of the CB, PCH and CHBT series

may be said that non-additivities of contributions to the mean polarisability brought about by these two kinds of ring are mutually comparable.

Another effect, however, is established when a —CN group is substituted by an —NCS group. In this case the experimental value of the rise in mean polarisability (4.8 Å^3) is higher than the value calculated from additivity of polarisability of bonds (3.8 Å^3). It must be supposed that the π-electron conjugation of the phenyl ring with the —NCS group affects polarisability more strongly than that with

TABLE II

The effect of substitution of the —CN group by the —NCS group and of the phenyl ring by the cyclohexyl ring upon the molecular polarisabilities of mesogens

Substitution	$\delta\alpha$ (Å^3)[a]	$\delta\alpha_l$ (Å^3)	$\delta\alpha_t$ (Å^3)
	-0.57 ± 0.02	-4.56 ± 0.06	1.42 ± 0.06
—CN → —NCS	4.82 ± 0.02	9.0 ± 0.6	2.7 ± 0.3

[a] 1 Å^3 ≡ 1.11×10^{-40} C^2 m^2 J^{-1}

the —CN group. An analysis of changes in longitudinal α_l and transverse α_t polarisabilities leads us to the conclusion that they are mainly caused by non-colinearity of the long axes of the phenylcyclohexyl units with the axes of their terminal groups, —CN or —NCS. The axes ought to form an angle of *ca.*25°.

The effective values of components μ_l and μ_t of dipole moments of molecules may be calculated from values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for any temperature. For that purpose use should be made additionally of

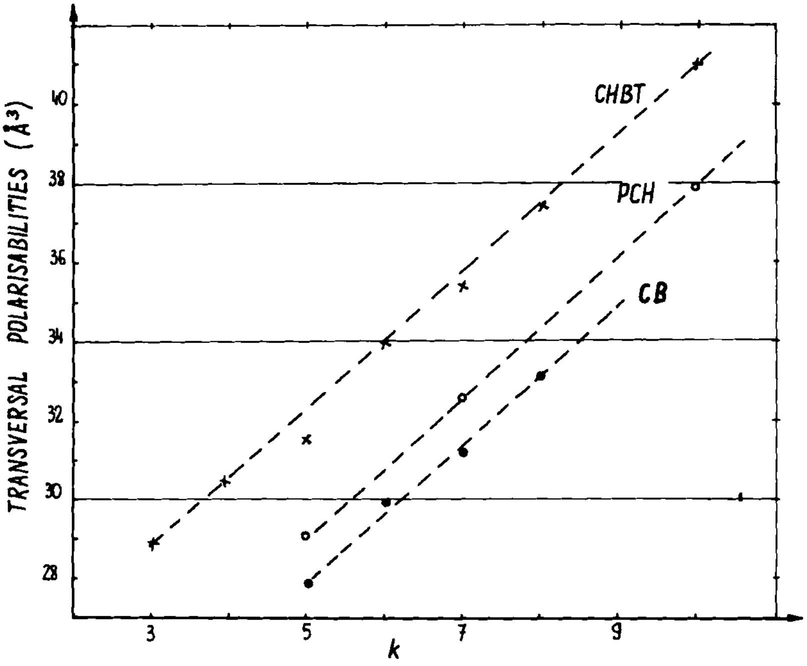


FIGURE 2 Transverse polarisabilities of the CB, PCH and CHBT series

TABLE III

Mean values of the dipole moments and of their orientation angles for the CB, PCH and CHBT series

Series	μ (10^{-30}C m)	μ_l (10^{-30}C m)	μ_t (10^{-30}C m)	β (°)
CB	10.8 ± 0.3	10.8 ± 0.3	0	0
PCH	10.0 ± 0.5	8.9 ± 0.1	4.1 ± 0.5	25 ± 2
CHBT	8.8 ± 0.4	8.1 ± 0.3	3.5 ± 0.6	23 ± 3

10^{-30}C m = 0.3 D

the dynamic polarisability, as well as of the order parameter, both determined from the refractive indices. If any polar compound forms associates with the dipole moments of the molecules situated parallel, it would be expected that with an increase in temperature, the parallel component of the effective dipole moment ought to grow. That would be a result of thermal breakdown of associates. Such an effect was established, e.g. for members of the CB series.[8] On the other hand, this effect has not been observed for any nematic studied in the CHBT series. This is evidence for absence of antiparallel association of the molecules in the nematics of this series. This is also consistent with the results of X-ray structural studies by Dabrowski *et al.*[9]

The above conclusion is also confirmed by the average values of effective dipole moments for the three series under study. They are collected in Table III. Thus, for the CB and PCH series, the total dipole moments are visibly lower than the dipole moment of the —CN group (13.5×10^{-30} C m), whereas for the CHBT series, the moment is comparable with the dipole moment of the —NCS group.

The difference between the dipole moments of the CB and PCH series determines the order of the effect on the dipole moment of π-electron conjugation between the phenyl ring carrying the alkyl group in the CB with the residue of the molecule. Table III shows that this is a slight effect. On the other hand, a strong effect of substituting a phenyl ring by a cyclohexyl ring consists in the appearance of a non-colinearity of the vector of the dipole moment in the mesogen with its long axis. The angle β, evaluated here, between these two directions is in agreement with the angle obtained from the analysis of the polarisability of the molecules. Both results are in accord in indicating that even when only one cyclohexyl ring is introduced next to the alkyl chain, the orientation of the long axis of the molecule in relation to its rigid core is changed.

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