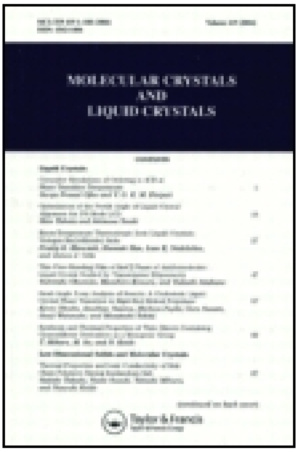

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Phase Transition and Physical Properties of a Binary Mixture Showing Enhanced Smectic Phase

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PHASE TRANSITION AND PHYSICAL PROPERTIES OF A BINARY MIXTURE SHOWING ENHANCED SMECTIC PHASE.

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Abstract Binary mixture of 4 octyloxy- 4'-cyano-biphenyl (8OCB) and 4-n-hexyl phenyl 4-n' pentyloxy benzoate (ME 50.6) shows enhanced smectic A phase, where 8OCB has both nematic and smecticA phases and ME 50.6 has only nematic phase. In the present paper we report the phase diagram, refractive indices, densities and orientational order parameters of different binary mixtures of 8OCB/ME 50.6 throughout the entire composition range. Birefringence as well as density values show minima with mole fraction of 8OCB. Order of smectic to nematic phase transition has been discussed.

INTRODUCTION

From the observation of the evolution of liquid crystalline properties through the investigation of binary phase diagrams, it has been found that smectic A phase can be strongly stabilized in mixtures[1]. The maximum transition temperature is increased compared to the corresponding temperature in the pure state, hence enhancing the smectic phase. Sometimes, it has been observed that although none of the pure compounds is smectic, yet the mixtures of these compounds often show so-called "injected smectic phase"[2-5].

Most of the cases[2-5] these phenomena have been observed in mixtures of two rod like molecules, one having terminal polar group and other being terminal non-polar and in only few cases[6], with mixtures of two non-polar mesogens.

A theoretical interpretation of this phenomenon has been given by considering complex formation between the two kinds of molecules[7] which implies an important influence of the chemical structure. The increase of transition temperature in mixtures is clearly related to the large variation of the layer spacing. From our earlier studies[8,9] it has been observed that there is a decrease in layer spacing near the equimolar concentration of two binary mixtures showing injected smectic phase. The possible cause may due to the specific interaction between the mixture molecules which stabilize the injected smectic phase but with lower orientational order as observed from x-ray and refractive index measurements[9].

We have obtained an enhanced smectic phase from the binary mixtures of 4 octyloxy-4'-cyanobiphenyl (8OCB) and 4-n-hexyl phenyl 4-n' pentyloxy benzoate (ME 50.6). 8OCB has both nematic and smectic phases, while ME 50.6 has only nematic phase.

In the present paper we report the phase diagram, refractive indices (n_o,n_e), densities and orientational order parameters of the binary mixtures 8OCB/ME 50.6 throu--ghout the entire composition range. To understand the unusual behaviour of this system we have also studied the trends of the different physical parameters with molar concentration.

EXPERIMENTAL

The materials 8OCB and ME50.6 were obtained from E. Merck, U.K. and were used without further purification. After mixing thoroughly, each mixture was heated to a temperature slightly above the clearing temperature and kept at that temperature for about 24 hours to ensure the formation of homogeneous mixtures. The phase diagram and transition temperatures were obtained by observing textures under crossed polarizers with a polarizing microscope equipped with a hot stage (Mettler FP 80/82). The refractive indices (n_o,n_e) for three wave lengths λ=6907Å, 5780Å and 5461Å were measured within ± 0.001 with the thin prism method. The densities of the mixtures at different temperatures were determined within 0.1%. The experimental details have been reported by Zeminder et al[10].

RESULTS AND DISCUSSIONS

The phase diagram of this system (8OCB/ME50.6) is shown in figure 1. As mentioned in the introduction, sample 8OCB shows both nematic and smecticA phases and ME50.6 shows only nematic phase. For mixtures having x (the mole fraction of 8OCB) between 0.25-0.45 nematic phase is completely suppressed. Only a little amount of 8OCB (8%) can induce smectic A phase. This type of enhanced smectic phase behaviour has been reported earlier by other workers[11]. Maximum smectic to isotropic transition temperature (82^{o}C) occurs for mixtures having x ≈ 0.37. The texture of the pure compounds and their mixtures are typical marbled-type texture in the nematic phase and focal conic texture in the smectic phase. In the co-existing smectic-isotropic phase we have found a mixture of bâtonnet and isotropic droplets. The mixtures can be supercooled by about 20^{o}C in the mesomorphic phase before solidifying.

The variations of refractive indices (n_o,n_e) for λ=5780Å with temperature are shown in figure 2. At other two wavelengths the variations are similar but not shown in the figure. To have a clear picture of the phase transition we have plotted optical birefringence ($\Delta n = n_e - n_o$) as a function of temperature in figure 3. In figure 4 we have plotted results of our density measurements with temperature.

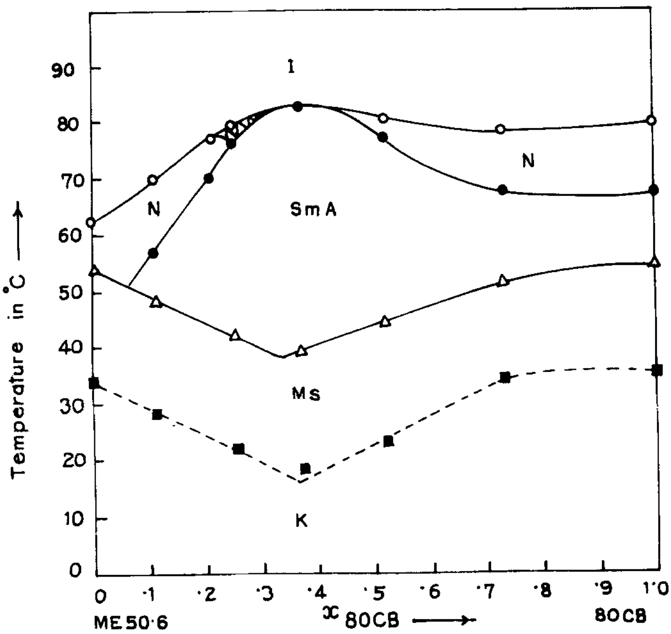

FIGURE 1. Phase diagram for the binary mixtures of 4 octyloxy-4'-cyanobiphenyl(8OCB) and 4-n-hexyl phenyl 4-n' pentyloxy benzoate (ME50.6). I isotropic; N nematic; SmA smecticA; Ms metastable phase (solid while heating and mesomorphic while cooling); K solid phase; shaded region represents co-existing SmA and isotropic phase. x_{8OCB} is the mole fraction of 8OCB.

Both the birefringence and density values of ME50.6 are lower than those obtained from 8OCB by Mitra et al[12]. This is expected because it is well known that cyanobiphenyls have greater birefringence than ester mesogens. Mixtures 1 and 2 (mole fraction of 8OCB = 0.25 and 0.37 respectively) have only smectic phase whereas mixtures 3 and 4 (x= 0.52 and 0.73 respectively) have both smectic and nematic phases. There is a small smectic -isotropic co-existing

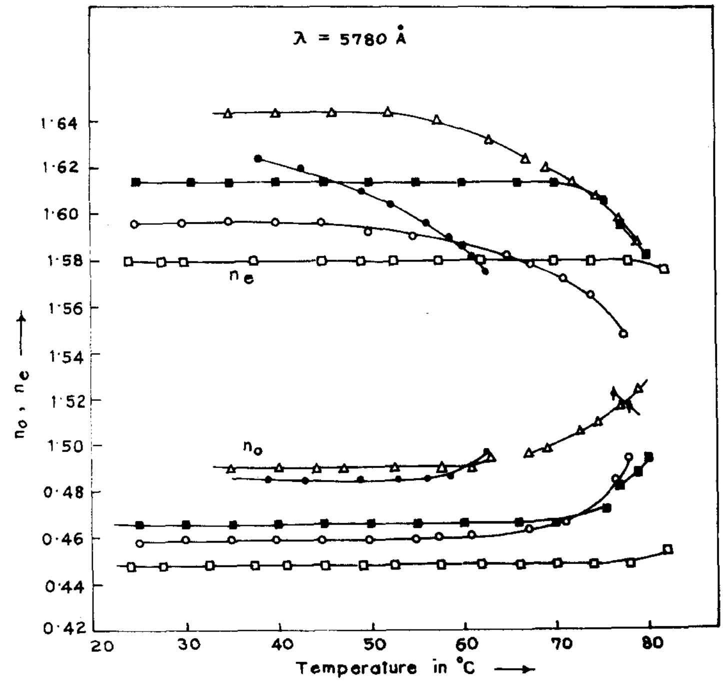

FIGURE 2. Refractive indices (n_o,n_e) as a function of temperature for different mixtures and pure compound ME 50.6. ● ME 50.6; ○ mixture 1; □ mixture 2; ■ mixture 3; Δ mixture 4; ⧫ n_{iso} values in co-existing (smectic/isotropic) phase of mixture 1.

region present in mixture 1. The change of birefringence as well as density values seems to be continuous for mixture 4 (mole fraction of 8OCB = 0.73) at the smectic-nematic phase transition which indicates a weakly first order or second order phase transition. On the other hand mixture 3 (x=0.52) shows a sharp discontinuity of birefringence and density values at the smectic/nematic phase transition temperature, hence it appears to be of the first order. Both the birefringence and density values change sharply with temperature in the coexisting smectic-isotropic region of mixture 1(x=0.25). We have been able to observe three refractive indices n_o, n_e and n_{iso} simultaneously in this phase and temperature dependence of n_{iso} is large within the co-existing region. Again in mixture 2 both the refractive indices (n_o,n_e) do not change with temperature, hence, Δn remains almost constant throughout the entire mesomorphic range (except near the isotropic transition). Birefringence in mixtures 1 and 2 in smecticA phase is lower than those found in mixtures 3 and 4. From our density values it is clear that temperature dependences of density values in smectic phase is much higher than those obtained from pure ME 50.6 and 8OCB. For most of the mixtures density values changes sharply with temperature in the smecticA phase except near T_{SN}. It is to be noted that

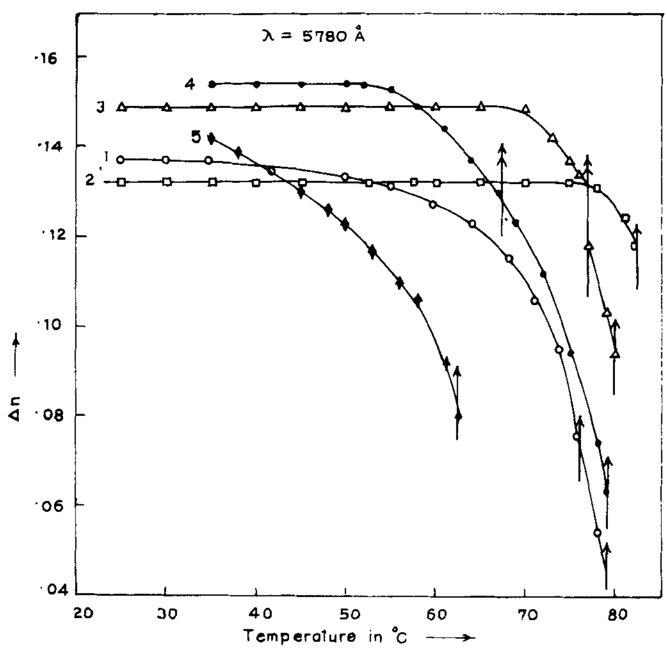

FIGURE 3. Birefringence ($\Delta n = n_e - n_o$) as a function of temperature for different mixtures and pure compound ME 50.6. ◆ ME 50.6 (5); o mixture1; □ mixture 2; △ mixture 3; ● mixture 4; ↑ N-I or SmA-I transition; ↟ SmA-N transition.

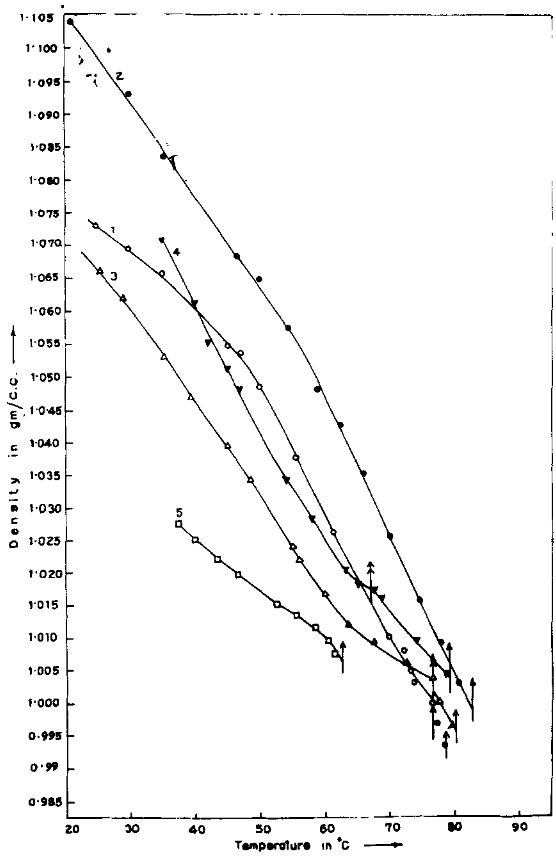

FIGURE 4. Density (ρ) as a function of temperature for different mixtures and pure compound ME 50.6. □ ME50.6 (5); O mixture1 (● coexisting SmA and isotropic phase); ● mixture 2; Δ mixture 3; ▼ mixture 4; ↑ N-I or SmA-I transition; ↟ SmA-N transition.

temperature variation of density is largest in mixture 2, which has the highest mesomorphic to isotropic transition temperature.

In figure 5, we have plotted Δn at $T=35^{o}C$ and also n_{iso}, isotropic refractive index (measured just above the clearing temperature), as a function of mole fraction of 8OCB. Birefringence as well as n_{iso} change continuously with mole fraction of 8OCB, having a broad minimum near $x \approx 0.38$.

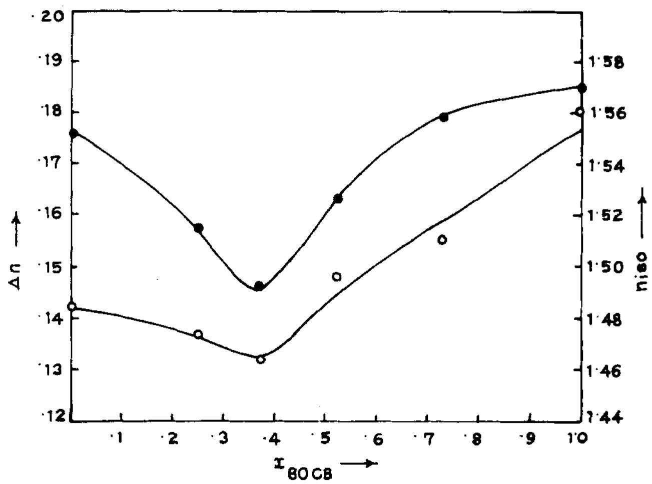

FIGURE 5. Birefringence (Δn) and n_{iso} plotted against mole fraction of 8OCB. ● n_{iso}; ○ Δn at $T = 35^{o}C$.

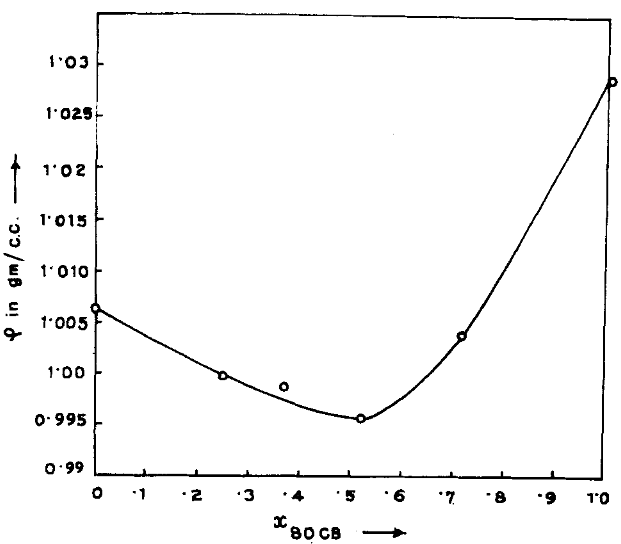

FIGURE 6. Density (ρ) just below the mesomorphic to isotropic transition temperature against mole fraction of 8OCB; continuous line drawn as a guide to the eye only.

In Figure 6 we have plotted density values in the mesomorphic phase, just below the mesomorphic to isotropic transition temperature against mole fraction of 8OCB. It is clear that density values near the clearing temperature shows a minimum near equimolar concentration.

Principal molecular polarizabilities (α_o, α_e) were measured from refractive indices (n_o, n_e) using Vuk's method[13] and also Neugebauer's relation[14]. The orien--tational order parameter $\langle P_2 \rangle$ was calculated by the relation

$$\langle P_2 \rangle = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$$

where α_e, α_o are effective polarizibilities for extraordinary and ordinary rays, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizibilities respectively parallel and transverse to the long axis of the molecule. Applying the extrapolation procedure of Haller et al[15] we have estimated $(\alpha_{\parallel} - \alpha_{\perp})$. In Figure 7 we have plotted the polarizibility anisotropy α_a =

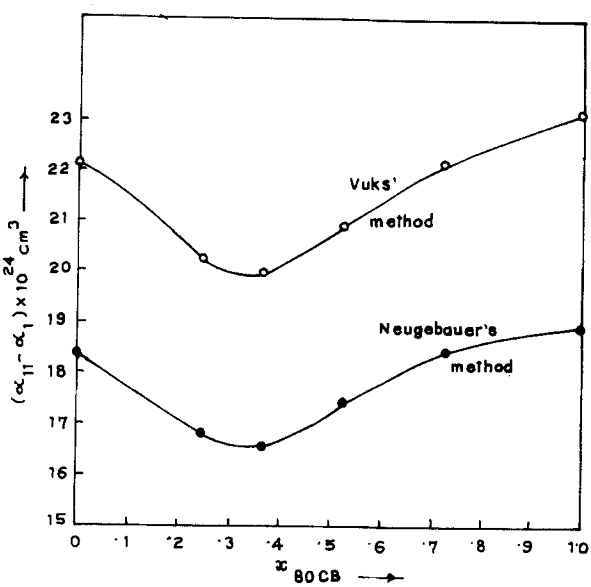

FIGURE 7. $(\alpha_{\parallel} - \alpha_{\perp})$ against mole fraction of 8OCB. o Vuk's method; ● Neugebauer's method.

$(\alpha_{\parallel} - \alpha_{\perp})$ values in pure sample ME 50.6 as well as different mixtures against mole fraction of 8OCB. α_a values for 8OCB obtained by Mitra et al[12] have also been included in this figure. Although polarizability anisotropy obtained from Haller's procedure is somewhat ambiguous, we have found a definite decrease of α_e near $x \approx 0.38$. Since anisotropy is almost proportional to the apparent molecular length, x-ray diffraction studies can give more information about this observation. We are not aware of x-ray measurements on the system reported here, but for a related cyanobiphenyl/ester mixture a minimum in layer spacing was found near the maximum in the enhanced smectic phase region[11]. This x-ray result do support the polarizability anisotropy values of the present work.

The order parameter values calculated using Vuk's[13] formula and Neugebauer's relations[14] agree quite well for all the mixtures as well as pure ME 50.6 in their respective phases. This may be due to the fact although α_o and α_e values are different in the two approaches, the variation of $(\alpha_e - \alpha_o)$ with temperature is more or less the same in the two cases[12]. Figure 8 shows the variation of $\langle P_2 \rangle$ values with temperature for the four mixtures and one pure compound ME 50.6. The orientational order parameter calculated from refractive index data at different wavelengths give essentially the same value.

Our experimental orientational order parameter values at the smecticA to nematic phase transition appears to be of the first order for mixture 3, while it is probably of the second order for mixture 4. In pure 8OCB the smectic to nematic transition is of the second order[16]. It is to be noted that mixture 4 contains largest fraction of 8OCB among the mixtures studied by us. Again $\langle P_2 \rangle$ values obtained in the co-existiong S_A-I region is substantially lower compared to those obtained at the adjacent smectic A phase. This is not entirely unexpected since in the co-existing region director fluctuations are quite large.

In mixture 2 the orientational orderparameter values increase with increasing temperature throughout the smectic phase except for a slight decrease just before smectic-isotropic transition temperature. This is not surprising because, Δn values in this case almost temperature independent whereas density values change rapidly with temperature, hence reducing the $\langle P_2 \rangle$ values with decreasing temperature.

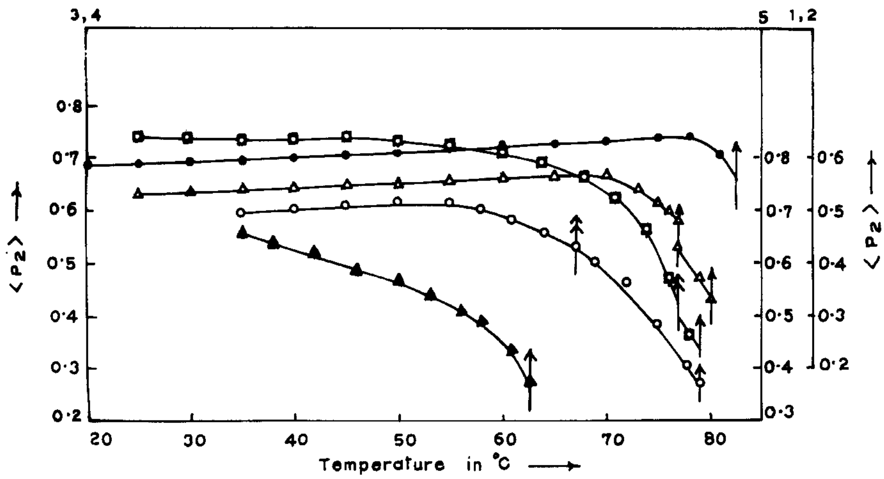

FIGURE 8. Order parameter $\langle P_2 \rangle$ as a function of temperature. ▲ ME50.6; □ mixture 1; ● mixture 2; Δ mixture 3; o mixture4; ↑ N-I or SmA-I transition; ↟ SmA-N transition.

Since for most of the mixtures the $\langle P_2 \rangle$ values are nearly constant over their smectic phases, we have not tried to fit these with McMillan's theory[17].

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REFERENCES

1. H. Sackmann and D. Demus, Z.Phys.Chem., 230, 285 (1965).
2. C. S. Oh, Mol.Cryst.Liq.Cryst, 42, 1 (1977).
3. D. A. Dunmur, R. G. Walker and P. Palffy-Muharoy, Mol.Cryst.Liq.Cryst, 122, 321 (1985).
4. M. J. Bradshaw and E. P. Raynes, Mol.Cryst.Liq.Cryst., 91, 145 (1983).
5. M. K. Das and R. Paul Phase Transitions, 1994 (in press).
6. M. Domon and J. Billard, J.Phys(Paris), 40, C3-413 (1979).
7. W. H. de Jeu, L. Longa and D. Demus, J.Chem.Phys, 84, 6410 (1986).
8. M. K. Das and R. Paul Phase Transitions, 1994 (in press).
9. M. K. Das , R. Paul and D. A. Dunmur, Communicated to Mol. Cryst. Liq. Cryst. (1994).
10. A. K. Zeminder, S. Paul and R. Paul, Mol. Cryst. Liq. Cryst, 61 191 (1980).
11. P. E. Cladis, Mol. Cryst. Liq. Cryst., 67, 177 (1981).
12. M. Mitra, S. Paul and R. Paul, Z.Naturforsch., 46a 858 (1991).
13. M. F. Vuks, Opt.Spestrosc.(USA), 20 361 (1954).
14. H. E. J. Neugebauer, Can.J.Phys., 32, 1 (1954).
15. I. Haller, H. A. Huggins, H. R. Lilienthal, T.R. McGuire, J.Phys.Chem., 77, 950 (1973).
16. M. A. Anisimov, E. E. Gorodetskii and V. M. Zaprudskii, Sov.Phys. USPEKHI, 24, 57 (1981).
17. M. L. McMillan, Phys.Rev., A4,1238 (1971); A6,936 (1972).