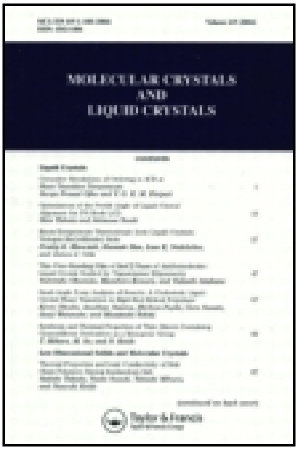


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Comparative X-Ray Diffraction Study of Two Liquid Crystalline 2,5-Disubstituted 1,3,4-Oxadiazole and 1,3,4-Thiadiazole Derivatives in Their Smectic Phases

Vladimir F. Petrov [a] , Takeyasu Tasaka [a] , Hiroaki Okamoto [a] , Shunsuke Takenaka [a] , Sofia I. Torgova [b] , Ludmila A Karamysheva [b] & Irina F. Agafonova [b]

[a] Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2557, Ube, Yamaguchi, 755-8611, Japan

[b] Organic Intermediates & Dyes Institute, B. Sadovaya 1/4, Moscow, 103787, Russia

Version of record first published: 24 Sep 2006

To cite this article: Vladimir F. Petrov, Takeyasu Tasaka, Hiroaki Okamoto, Shunsuke Takenaka, Sofia I. Torgova, Ludmila A Karamysheva & Irina F. Agafonova (2000): A Comparative X-Ray Diffraction Study of Two Liquid Crystalline 2,5-Disubstituted 1,3,4-Oxadiazole and 1,3,4-Thiadiazole Derivatives in Their Smectic Phases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 348:1, 73-78

To link to this article: http://dx.doi.org/10.1080/10587250008024797

Mol. Cryst. Liq. Cryst., Vol. 348, pp. 73-78
Reprints available directly from the publisher
Photocopying permitted by license only

A Comparative X-Ray Diffraction Study of Two Liquid Crystalline 2,5-Disubstituted 1,3,4-Oxadiazole and 1,3,4-Thiadiazole Derivatives in Their Smectic Phases

VLADIMIR F. PETROV[a*], TAKEYASU TASAKA[a], HIROAKI OKAMOTO[a], SHUNSUKE TAKENAKA[a], SOFIA I. TORGOVA[b], LUDMILA A KARAMYSHEVA[b] and IRINA F. AGAFONOVA[b]

[a]Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2557, Ube, Yamaguchi 755–8611, Japan and [b]Organic Intermediates & Dyes Institute, B. Sadovaya 1/4, Moscow 103787, Russia

(Received May 17, 1999; In final form July 08, 1999)

Abstract. X-ray diffraction study of two liquid crystalline 2,5-disubstituted 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives reveals the existence of a partially bilayered smectic Ad phase in the terminally bromo substituted derivatives, with the lower level of molecular overlapping in the formation of the dimer and more pronounced smectic fluctuations on the dimeric density wave observed for the former compound.

Keywords: X-ray diffraction; smectic; 1,3,4-oxadiazole; 1,3,4-thiadiazole

1. INTRODUCTION

It has been shown that the mesomorphic and physical properties of liquid crystals strongly depend on their molecular core structures.[1–11] As the mesophase stability is influenced by molecular packing[12], the investigation of intermolecular interactions, association phenomena, dipole-dipole correlations affecting the molecular packing could lead to a better understanding of liquid crystal properties.

---

[*] Author for correspondence.

It has been demonstrated that X-ray diffraction of the mesophases is one of the useful methods to study the association phenomena in the liquid crystals.[2, 3, 8, 10, 11, 13–19] It is well-known that the polar liquid crystals may exhibit a number of lamellar packings.[10, 14–22] Apart from the ordinary smectic A_1 phase with a period, d, approximately equal to the molecular length, L, there are bilayered smectics A_2 with the period $d \approx 2L$ and intermediate (partially bilayered) smectics A_d having the period d which is $L < d < 2L$. These phenomena are due to the specific nature of intermolecular interactions in polar liquid crystals, resulting in various effects of molecular association. Anti-parallel correlations between permanent and induced molecular dipoles influence the subtle balance between the attractive dispersion forces and the repulsive steric ones, and give rise to the structural packing of the S_{A1}, S_{A2} or S_{Ad} types.[23] Here we present the results of X-ray diffraction study of two terminally bromo substituted liquid crystalline 1,3,4-oxadiazole-2,5-diyl (OXA) and 1,3,4-thiadiazole-2,5-diyl (THIA) derivatives. The experimental results will be discussed in terms of influence of molecular core structure of liquid crystals on the structure of their smectic phases. The mesomorphic properties of these compounds have been reported earlier.[24]

2. EXPERIMENTAL TECHNIQUE

X-ray diffraction experiments were performed with a Rigaku-Denki RINT 2200 diffractometer, fitted with a Rigaku PTC-20A thermal controller, where CuKα ($\lambda = 1.540$ Å) was used as the X-ray source. The reflection angle was calibrated by the examination of both left and right angles. Samples filled in the quartz capillaries (d = 1 mm) were oriented by a constant magnetic field (480 G). The samples were placed along the goniometer axis so that the counter movement in the recording plane allowed us to scan the nematic and smectic A reciprocal lattice mode along q ($q = 2\pi / d$ is the reciprocal space vector), i.e. in the direction parallel to the director **n**.

3. EXPERIMENTAL RESULTS AND INTERPRETATION

The phase transition temperatures and enthalpies of compounds **1–2**[24]; their molecular lengths L calculated by MOPAC AM1 method[25]; the layer spacing of the smectic A phase and a period of the fluctuation density wave d in the nematic phase obtained from X-ray diffraction profiles; the intensity of X-ray scattering I and corresponding correlation length ζ {calculated from the angular width of the intensity profile at half-height $\Delta(2\Theta)^{10}$} ; and the ratios d / L are presented in table I. The values of ratios d / L >1 indicate the formation of a partially bilayered smectic A phase – A_d in compounds **1, 2**. Based on these results, the antiparallel molecular arrangements supported by the theoretical models[19] can be proposed for these liquid crystals.

The data collated in table I reveal that 1,3,4-oxadiazole-2,5-diyl derivative **1** exhibits the smectic Ad phase with higher ratio d / L (lower level of molecular overlapping in the formation of the dimer) and shows the higher intensity of X-ray scattering and correlation length in comparison with those of the corresponding 1,3,4-thiadiazole-2,5-diyl derivative **2**.

The temperature dependences of the layer spacing d in the smectic A phases of compounds **1, 2** are shown in Figure 1. For the 1,3,4-oxadiazole-2,5-diyl derivative **1** d shows the decreasing behavior with saturation close to the melting point, while for the 1,3,4-thiadiazole-2,5-diyl derivative **2** d is almost independent of the temperature. This difference in the temperature behaviour of the layer spacing of compounds **1** and **2** is probably due to the different role of molecular dimers in the formation of layers.[10]

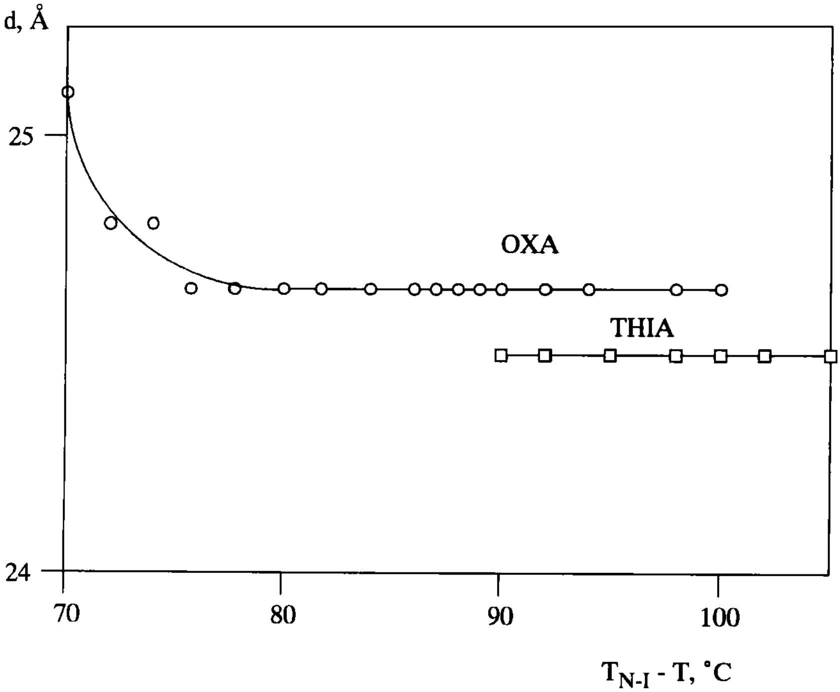
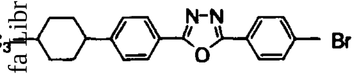
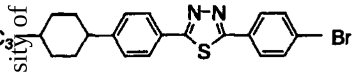


FIGURE 1 Temperature dependences of the layer spacing d for OXA (○) and THIA (□). The lines are guides for the eye

ABLE I Physico-chemical properties of liquid crystalline 2,5-disubstituted 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives

Compound	*Abbrev.*	*Phase transitions, °C*	*L, Å*	*d^*, Å*	*d/L*	*I^*, count*
	OXA	Cr 122 S_{Ad} 152 N 214 I	20.59	24.66	1.20	1727
	THIA	Cr 140 S_{Ad} 185 N 245 I	21.45	24.52	1.14	60

90 °C

The temperature dependences of the correlation length for compounds **1, 2** presented in Figure 2 show the usual increasing behaviour with decreasing the temperature, with the highest rate and lower value recorded for compound **2** (compare the data for these compounds at the same relative temperature $T_{N\text{-}I} - T$).

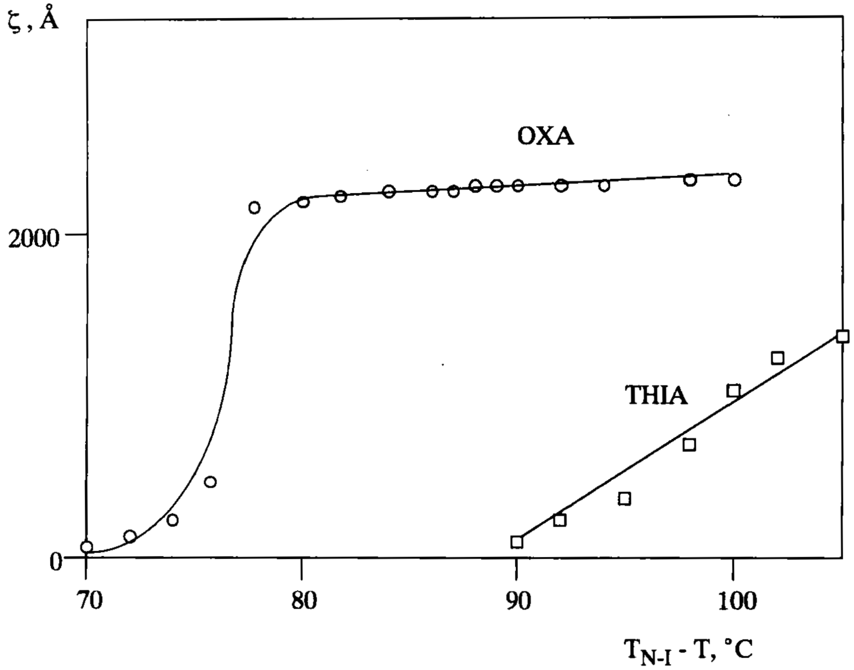


FIGURE 2 Temperature dependences of the correlation length ζ for OXA (○) and THIA (□). The lines are guides for the eye

The presented results of X-ray diffraction study of two liquid crystalline 2,5-disubstituted 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives show the different influence of the structures of the 1,3,4-oxadiazole-2,5-diyl and 1,3,4-thiadiazole-2,5-diyl fragments[26, 27] on the intra- and intermolecular interactions [27] leading to the observed molecular arrangements. Similar results have been found for other liquid crystalline derivatives.[2, 3, 10, 11, 17–19]

4. CONCLUSION

The results of X-ray diffraction study of two liquid crystalline 2,5-disubstituted 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives reveal the strong influence of their molecular core structures on the structure of their smectic phases resulting in the formation of a partially bilayered smectic Ad phase, with the lower level of molecular overlapping in the formation of the dimer and more pronounced smectic fluctuations on the dimeric density wave recorded for the former compound.

References

1. G. W. Gray, *Advances in Liquid Crystals*, Vol. 2, (Academic Press Inc., New York and London, 1972).
2. V. F. Petrov, S. A. Ivanov, M. F. Grebenkin, and A. I. Pavluchenko, *Rus. J. Phys. Chem.*, **64**, 421(1990).
3. V. F. Petrov, M. F. Grebenkin, A. I. Pavluchenko, and N. I. Smirnova, *Rus. J. Phys. Chem.*, **65**, 447(1991).
4. L. A. Karamysheva, I. F. Agafonova, R. Kh. Geivandov, and V. F. Petrov, *Liq. Crystals*, **10**, 875(1991).
5. A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, M. F. Grebyonkin, and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, **209**, 155 (1991).
6. A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, Yu. A. Fialkov, S. V. Shelyazhenko, and L. M. Yagupolsky, *Mol. Cryst. Liq. Cryst.*, **209**, 225(1991).
7. A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, Y. A. Fialkov, S. V. Shelyazhenko, M. Schadt, and R. Buchecker, *Mol. Cryst. Liq. Cryst.*, **265**, 41(1995).
8. V. F. Petrov, A. I. Pavluchenko, and N. I. Smirnova, *Mol. Cryst. Liq. Cryst.*, **265**, 47(1995).
9. V. F. Petrov, Liq. Crystals, **19**, 729(1995).
10. B. I. Ostrovskii, A. I. Pavluchenko, V. F. Petrov, and M. A. Saidachmetov, *Liq. Crystals*, **5**, 513(1989).
11. M. F. Grebyonkin, V. F. Petrov, and B. I. Ostrovsky, *Liq. Crystals*, **7**, 367(1990).
12. M. A. Osman and L. Revesz, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 41(1982).
13. F. Hardouin, A. M. Levelut, *J. Physique*, **41**, 41(1980).
14. A. M. Levelut, R. J. Tarento, F. Hardouin, M. F. Achard, and G. Sigaud, *Phys. Rev. A*, **24**, 2180(1981).
15. B. I. Ostrovskii, B. M. Bolotin, and M. A. Saidachmetov, *Liq. Crystals*, **5**, 525(1989).
16. G. I. Brownsey and A. J. Leadbetter, *Phys.* Rev. *Lett.*, **44**, 1608(1980).
17. T. A. Lobko and B. I. Ostrovskii, *Mol. Mats.*, **1**, 99(1992).
18. B. I. Ostrovskii, *Liq. Crystals*, **14**, 131(1993).
19. T. A. Lobko, B. I. Ostrovskii, A. I. Pavluchenko, and S. N. Sulianov, *Liq. Crystals*, **15**, 361(1993).
20. F. Hardouin, A. M. Levelut, M. F. Achard, and G. Sigaud, *J. Chim. Phys.*, **80**, 53(1983).
21. J. Prost and P. Barois, *J. Chim. Phys.*, **80**, 65(1983).
22. W. H. de Jeu, *Structural Incommensurability in Crystals, Liquid Crystals and Quasi-crystals*, edited by J. F. Scott (Plenum Press, New York, 1986).
23. J. O. Indekeu and A. N. Berker, *Physica A*, **140**, 368(1986).
24. L. A. Karamysheva, S. I. Torgova, I. F. Agafonova, V. F. Petrov, and S. Takenaka, *Proceedings of the Fifth International Display Workshops*, *IDW* '98, 7–9 December 1998, Kobe, Japan, p. 837.
25. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Steward, *J. Am. Chem. Soc.*, **107**, 3902(1985).
26. A. A. El-Azhary, *Spectrochimica Acta*, **51A**, 995(1995).
27. O. A. Ponomarev, Yu. N. Surov, N. S. Pivnenko, N. A. Popova, and I. A. Fedyunyaeva, *Chemistry of Heterocyclic Compounds*, **33**, 707(1997).