ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 5, pp. 839–840. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.V. Zuev, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 5, pp. 875–876.

LETTERS TO THE EDITOR

Synthesis and Photoluminescent Properties of Liquid Crystalline Derivatives of Bis-stilbene

V. V. Zuev

Institute of High-Molecular Compounds, Russian Academy of Sciences,
Bol'shoi pr. 31, St. Petersburg, 199004 Russia

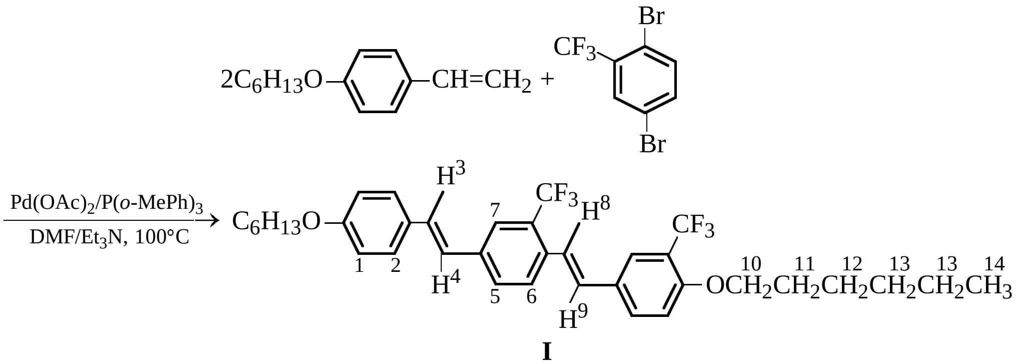
Received January 16, 2006

DOI: 10.1134/S1070363206050318

Development of modern cathode luminescent displays necessitates organic compounds capable of giving polarized luminescence on excitation. Such compounds include, for example, smectic liquid crystals with a high order parameters (up to 0.9) and, as a consequence, high molecular orientation in monodomen samples [1].

Using the Heck reaction we prepared bis-stilbene (**I**) in ~70% yield; therewith, the catalyst was generated in situ from equimolar amounts of palladium acetate and corresponding phosphine. According to the ^{1}H NMR spectrum (J 14.7 Hz), the double bonds in bis-stilbene are both *trans*. This result is not unusual with the Heck reaction which is performed at fairly high temperatures [2].

The resulting compound, being relatively low-melting (mp 72°C), forms a smectic mesophase (isotr°pization point 172°C). Because of the presence of terminal hexyl groups, compound **I** is readily soluble in dioxane, THF, methylene chloride, and chloroform.



I

The absorption maximum of compound **I** in dioxane is at 358 nm (ε 12 000). The photoluminescence maximum in dioxane is at 431 nm (Stock's shift ~70 nm). From the dioxane solution we deposited a film on a quartz plate. As is usual with films, the photoluminescence band of the film was shifted bathochromically and got broader (λ_{max} 460 nm).

To prepare oriented bis-stilbene samples, we used commercial polyamide-coated quartz plates with a series of parallel microgrooves made with a diamond cutter. A solution of compound **I** was applied on the plate, and it was subjected to a vacuum at 100°C for 1 day. We failed to obtain highly oriented samples (degree of polarization absorption 1.04). As a result, the degree of photoluminescence polarization was as low as 1.5, against 4.7–6.5 attainable with polymers [3].

1,4-Bis[2-[4-(*n*-hexyloxy)phenyl]vinyl]-2-(trifluoromethyl)benzene. A mixture of 1 g of 1,4-dibromo-2-(trifluoromethyl)benzene, 1.5 g of 4-*n*-hexylstyrene, 100 mg of palladium acetate, and 400 mg of tri-°-tolylphosphine in 30 ml of DMF and 10 ml of triethylamine was stirred under argon at 100°C for 3 days. After cooling, the reaction mixture was poured into 250 ml of ethanol. The precipitate that formed was filtered off and recrystallized first from ethanol and then from toluene. Yield 1.3 g (71%). IR spectrum (KBr), ν, cm^{-1}: 2935, 2864, 1606, 1514, 1294, 1253, 1176, 1161, 1049, 957, 835. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.90 d (4H, H^1, *J* 8.1), 7.45 d (4H, H^2, *J* 8.1), 6.96 d (1H, H^3, *J* 14.7), 7.34 d (1H, H^4, *J* 14.7), 7.61 d (1H, H^5, *J* 8.1), 7.75 d (1H, H^6, *J* 8.1), 7.74 s (1H, H^7), 7.45 d (1H, H^8, *J* 14.7), 6.90 d (1H, H^9, *J* 14.7), 3.98 t (4H, H^{10}, *J* 6.6), 1.77–1.84 m (4H, H^{11}), 1.35–1.44 m (12H, $H^{12–14}$), 0.94 t (6H, H^{15}, *J* 6.6). Found, %: C 73.11; H 7.50. $C_{35}H_{41}F_3O_2$. Calculated, %: C 73.66; H 7.24.

The IR spectrum was obtained on a Bruker Vertex instrument. The 1H NMR spectrum was recorded on a Bruker MSL-400 spectrometer (400 MHz). The UV spectrum was taken a Specord M-40 spectrophotometer in dioxane (c 1×10^{-5} M) and in film. The luminescence spectra were measured on an LS-100-3 spectrofluorimeter (PTI, Canada) in dioxane (c 1×10^{-5} M). The temperatures of phase transitions were measured on Botius hot stage and a Perkin–Elmer Pyris-1 differential scanning calorimeter, heating rate 10 deg min^{-1}. Tri-*o*-tolylphosphine and 4-*n*-hexylstyrene were purchased from Aldrich and 1,4-dibromo-2-(trifluoromethyl)benzene, from Lankaster.

REFERENCES

1. Gray, G.W. and Goodby, J.W., *Smectic Liquid Crystals–Textures and Structure*, Glasgow: Wiley, 1984.
2. Shul’pin, G.B. and Shilov, A.E., *Chem. Rev.*, 1997, vol. 97, no. 4, p. 2879.
3. Grell, M. and Bradley, D.D.C., *Adv. Mater.*, 1999, vol. 11, no. 11, p. 895.