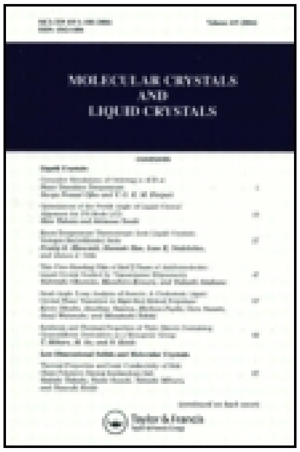

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Nitration of Triphenylene Discotics: Synthesis of Mononitro-, Dinitro- and Trinitro-Hexaalkoxy Triphenylenes

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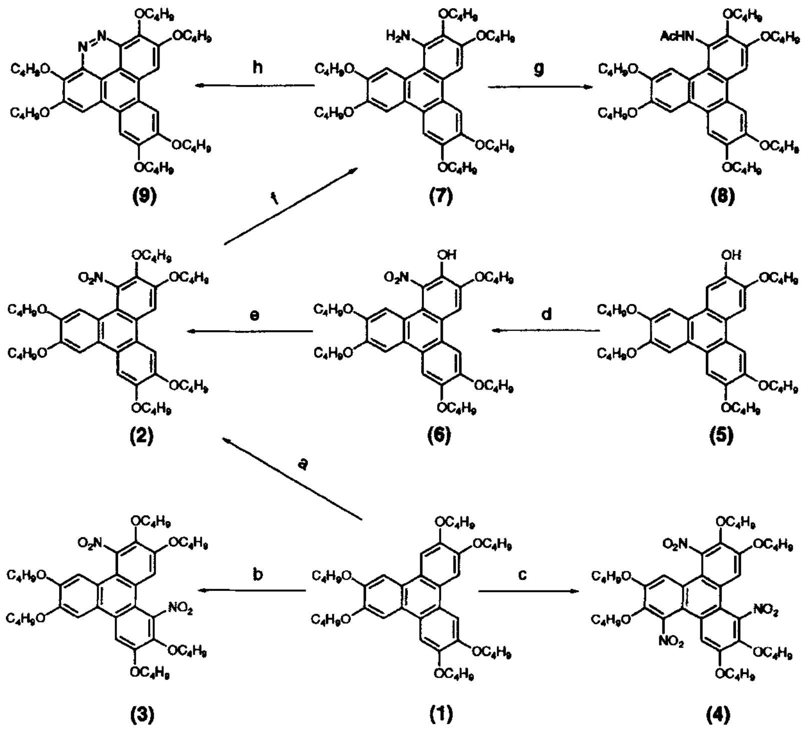
Nitration of hexaalkoxytriphenylene has very recently been reported to produce exclusively the 1-nitro-hexaalkoxytriphenylene. We have found that nitration of such discotics is not restricted to only one ring of triphenylene; all the three rings can be nitrated successively to produce mononitro-, dinitro- and trinitro-hexaalkoxytriphenylenes. These nitro-triphenylenes are valuable precursors to several other triphenylene derivatives. Mononitration of monohydroxy-penta-alkoxytriphenylene gives the monohydroxy-mononitro derivative, an extremely important precursor to functionalized triphenylene polymers.

Keywords: Discotic liquid crystals; triphenylene; nitration; nitro-triphenylene

The potential use of discotic liquid crystals [1] as quasi-one-dimensional conductors [2], photoconducting systems [3], ferroelectrics [4], light emitting diodes [5], photovoltaic solar cells [6], optical data storage devices [7], hybrid computer chips for molecular electronics [8], etc., are attracting considerable attention. Triphenylene based discotic liquid crystals are extensively studied for their one-dimensional conducting [2], photoconducting [3] and one-dimensional energy transfer [9] properties.

Most of the triphenylene discotic liquid crystals are colorless, low fluorescent materials and thus limiting their use in many applications. In order to induce molecular dipole and color, the Boden group has recently nitrated triphenylene discotics [10]. In an effort to enhance fluorescence as well as the mesogenity of triphenylene discotic liquid crystals, we have synthesized a number of new monofunctionalized triphenylene discotics bearing conjugative electron withdrawing substituents attached directly to the triphenylene core [11, 12]. Direct nitration of triphenylene discotics to produce functionalized triphenylene derivatives having lateral dipole moment, color, etc., is an attractive approach. Electrophilic aromatic substitution in unsubstituted triphenylene is directed by steric and electronic effects. Substitution at β-position or 2-position is favored compared to α-or 1-position presumably owing to steric hindrance effect [13]. However, the electronic effect plays a major role in the nitration of triphenylene and results a mixture of 1-nitro and 2-nitro triphenylene [13]. During the course of low-symmetry, fluorescent triphenylene synthesis, when we nitrated 3,6,7,10,11-pentaalkoxytriphenylene, nitration occurs preferentially in the sterically hindered 4-position [11]. Evidently, electronic effects dominate in the nitration of alkoxytriphenylenes. This prompted us to look into the nitration of triphenylene discotics more carefully.

When we nitrated hexabutyloxytriphenylenes (H4TP) as reported [10], the major mononitro- product was contaminated with a minor product that was isolated by column chromatography and characterized as the dinitro derivative of H4TP from its spectral analysis. When the concentration of HNO_3, time and temperature of the reaction was increased, formation of trinitro- derivative starts in addition to the dinitro- derivative as the major product. About 50% of the dinitro- and 10% of the trinitro-compound can easily be isolated from this mixture. Efforts to push the reaction towards trinitro- derivative by using excess HNO_3 and longer time yielded only a maximum of about 25% of the trinitrated product. However, this situation changed dramatically when we changed the solvent system from ether-acetic acid to dichloromethane–nitromethane and the trinitration is completed within 15 min at room temperature in very high yield. This trinitration proceeds with high regioselectivity to give exclusively one isomer having C3 symmetry. Use of 1 equivalent of HNO_3 gives almost quantitatively the mononitro-H4TP in this solvent system and the formation of dinitro- can be regulated by the amount of nitric acid. Mono nitration of monohydroxy-pentabutyloxytriphenele (**5**), occurs as expected at 1-position to give monohydroxy-mononitro-pentabutyloxytriphenylene (**6**), characterized from detailed spectral analysis and by its conversion to (**2**). The mononitro–monohydroxy derivative (**6**) is an extremely valuable intermediate as the functionalities like hydroxy-group can be further utilised to prepare a variety of other derivatives, e.g. acrylates, vinyl ethers, etc., having potential for the preparation of functionalized liquid crystal polymers.



SCHEME 1

Nitro-triphenylenes are key precursors to several other derivatives like amino-, mono- and di-alkylamino, acylamino-, azo-, etc. For instance, the mononitro-H4TP was easily reduced to amino- derivative (7) with hydrazine and palladium or with nickel chloride and sodium borohydride. The amino- derivative was readily converted to acylamino- (8) with acetic anhydride in pyridine and to α,α′-diazo compound (9) by diazotization. All the products were purified by column chromatography over silica gel and characterized by their spectra analysis. Mesophase behaviors were established by polarizing microscope and DSC. Compounds 2, 8 and 9 exhibited D_h-like mesophase texture and very much resembles with that reported [10]. The above mentioned chemistry works well with other hexaalkoxytriphenylenes and the results will be published in due course.

Spectral Data and Phase Behavior

MS Data: M + . (**2**): 705.2; (**3**): 750.2; (**4**): 795.1; (**5**): 604.3; (**6**): 649.1(**7**): 675.1; (**8**): 717.3; (**9**): 687.4

1HNMR data: $CDC1_3$, δ(**2**): 7.82, s, 1H; 7.71, s, 1H; 7.68, s, 2H; 7.41, s, 1H, 4.17, m, 10H; 4.01, t, 2H; 1.8–1.4, m, 24H; 0.94, m, 18H. (**3**): 7.71, s, 1H; 7.59, s, 1H; 7.48, s, 1H; 7.35, s, 1H; 4.14, t, 8H; 4.03, t, 4H; 1.8–1.4, m, 24H; 0.95 m, 18H. (**4**): 7.48, s, 3H; 4.17, t, 6H; 4.01, t, 6H; 1.8, m, 6H; 1.7, m, 6H; 1.45, m, 12H; 0.93, m, 18H. (**5**): 7.89, s, 1H; 7.76, s, 4H; 7.71, s, 1H; 5.83, m, 1H; 4.19, m, 10H; 1.8–1.5, m, 20H; 0.97, m, 15H. (**6**): 7.82, s, 1H; 7.77, s, 1H; 7.76, s, 1H; 7.70, s, 1H; 7.40, s, 1H; 6.48, s, 1H; 4.23, m, 8H; 4.08, t, 2H, 1.90, m, 10H; 1.56, m, 10H; 1.03, m, 15H. (**7**): 8.74, s, 1H; 7.76, s, 1H; 7.72, s, 1H; 7.70, s, 1H; 7.31, s, 1H; 4.12, m, 12H; 1.8, m, 12H; 1.5, m, 12H; 0.95, m, 18H. (**8**): 8.67, s, 1H; 8.55, s, 1H; 7.7, m, 5H; 4.14, m, 12H; 2.3 and 1.8, s, 3H; 1.25–1.6, m, 24H; 0.97, m, 18H. (**9**): 8.33, s, 2H; 7.87, s, 2H; 4.65, t, 4H; 4.33, t, 4H; 4.23, t, 4H; 1.92, m, 12H, 1.58, m, 12H; 0.97, m, 18H.

Thermal behavior (T/°C): (**2**) Cr 61.2 D_h 141.3 i (**3**) Cr 107 i (**4**) Cr 142 i (**5**) Cr 108 i (**6**) Dec. above 106 (**7**) Cr 102 i (**8**) Cr 132.9 D_h 172.1 i (**9**) Cr 193.1 D_h 280.1 i.

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References

[1] For a brief review of discotics see S. Chandrasekhar, *Liq. Cryst.*, **14**, 3 (1993); see also S. Chandrasekhar and S. Kumar, *Science Spectra*, (**8**), 66 (1997).

[2] N. Boden, R. J. Bushby, J. Clements, M. V. Jesudason, P. F. Knowles and G. Williams, *Chem. Phys. Lett.*, **152**, 94 (1988); N. Boden, R. J. Bushby and J. Clements, *J. Chem. Phys.*, **98**, 5920 (1993); N. Boden, R. J. Bushby, A. N. Cammidge, J. Clements and R. Luo, *Mol. Cryst. Liq. Cryst.*, **261**, 251 (1995); N. Boden, R. C. Borner, R. J. Bushby and J. Clements, *J. Am. Chem. Soc.*, **116**, 10807 (1994) and references therein.

[3] a) D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and K. Siemensmeyer, *Phys. Rev. Lett.*, **70**, 457 (1993); b) D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and K. Siemensmeyer, *Ber. Bunsenges. Phys. Chem.*, **97**, 1366 (1993); c) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, W. Paulus, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Adv. Mater.*, **7**, 276 (1995); d) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Nature*, **371**, 141 (1994); e) J. Simmerer, B. Glusen, W. Paulus, A. Kettner, P. Schuhmacher, D. Adam, K. H. Etzbach, K. Siemensmeyer, J. H. Wendorff, H. Ringsdorf and D. Haarer, *Adv. Mater.*, **8**, 815 (1996).

[4] H. Bock and W. Helfrich, *Liq. Cryst.*, **18**, 387 (1995).

[5] J. Simmerer, P. Schuhmacher, K. Siemensmeyer, D. Funhoff, D. Adam, W. Paulus, H. Ringsdorf, D. Haarer, communicated (personal communication).

[6] B. A. Gregg, M. A. Fox and A. J. Bard, *J. Phys. Chem.*, **94**, 1586 (1990).

[7] C. Y. Lin, H. L. Pan, M. A. Fox and A. J. Bard, *Science*, **261**, 897 (1993); M. A. Fox, A. J. Bard, H. L. Pan and C. Y. Lin, *J. Chin. Chem. Soc.*, **40**, 321 (1993).

[8] N. Boden, R. Bissell, J. Clements and B. Movaghar, *Liquid Crystals Today*, **6**, 1 (1996).

[9] D. Markovitsi, A. Germain, P. Millie, P. Lecuyer, L. K. Gallos, P. Argyrakis, H. Bengs and H. Ringsdorf, *J. Phys. Chem.*, **99**, 1005 (1995) and references therein.

[10] N. Boden, R. J. Bushby and A. N. Cammidge, *Mol. Cryst. Liq. Cryst.*, **260**, 307 (1995); N. Boden, R. J. Bushby and A. N. Cammidge, *Liq. Cryst.*, **18**, 673 (1995); N. Boden, R. J. Bushby, A. N. Cammidge and G. Headdock, *J. Mater. Chem.*, **5**, 2275 (1995).

[11] J. A. Rego, S. Kumar and H. Ringsdorf, *Chem. Mater.*, **8**, 1402 (1996).

[12] S. Kumar, P. Schuhmacher, P. Henderson, J. Rego and H. Ringsdorf, *Mol. Cryst. Liq. Cryst.*, **288**, 211 (1996).

[13] C. M. Buess and D. D. Lawson, *Chem. Rev.*, **313** (1960).