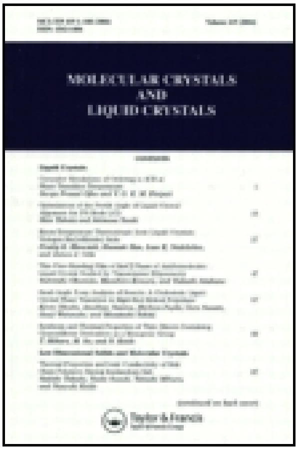

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Helioghromic Fulgides of Indole Species

Oieg Y. Fedorovskiy [a] , Yriy M. Chunaev [a] , Lidiya N. Kurkovskaya [a] , Nina M. Prghiyalgovskaya [a] & Nikolay O. Pirogov [a]

[a] Russian Chemical Technological University by D. I. Mendeleev, 125190, Moscow, Russia

To cite this article: Oieg Y. Fedorovskiy , Yriy M. Chunaev , Lidiya N. Kurkovskaya , Nina M. Prghiyalgovskaya & Nikolay O. Pirogov (1994): Helioghromic Fulgides of Indole Species, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 63-66

To link to this article: http://dx.doi.org/10.1080/10587259408037789

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 63–66
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

HELIOCHROMIC FULGIDES OF INDOLE SPECIES

OlEG Y.FEDOROVSKIY,YRIY M.CHUNAEV,LIDIYA N.KURKOVSKAYA
NINA M.PRGHIYALGOVSKAYA,NIKOLAY O.PIROGOV
Russian Chemical Technological University by
D.I.Mendeleev,125190 Moscow, Russia.

ABSTRACT For three fulgides photochromic behaviour was described.Also synthesis of this fulgides was described.

INTRODUCTION

Well-known heliochromic fulgides of furan, thiofen , pyrrol species present interest for utilization as photo-reactiv lenses[1,4]. In connection with it we decided to synthesize similar fulgides of indole species.

EXPERIMENTAL

^{1}H-NMR experiments (Bruker-200-SY) were carried out in deuterated chloroform and benzene with tetramethylsilan (TMS) as internal standard. We used EPS-3T "HITACHI" spectrophotometer to measure the absorption spectra.

RESULTS

From 1-methyl-2-formylindole and adamantylidensuccinate in toluene using sodium hydride by the Stobbe reaction fulgide 1 (λ=415nm) was synthesized which had E-configuration (fig.1) because the signal of vinyl's proton (7.60ppm) in H-spectrum appeared[6]. Short-time irradiation (λ=415nm) of the E-isomer 1 in toluene leads to Z-isomer 1 (λ=420nm).When we irradiate Z-isomer sunglight it reverses to the original form. Long-time irradiation (λ=415nm) towards the ring closure reaction to form cycle product 2 (λ=534nm). Cycle product 2 of indolic fulgide undergoes a termal 1,5-H shift to form 3 which under conditions of experiment (irradiation λ=415-420nm.,toluene, t=60°C) produced coloured form 4 (λ=552nm) reversibly.If we break irradiation and keep the solution in the dark during 3-4 hours, coloured product 4 transforms into cycle form 3. Heliochromic properties of compound 3 displays on sunglight irradiation during 0.5-1.5 sec., which produced reversibly red-cherry coloured form 4.The reverse reaction occurred in the dark.In ^{1}H-NMR-spectrum of coloured solution signals are observed from form 4,which can undergo E,Z-isomerisation on sunglight.By means of flash-photolysis there was determined the time of semitransformation for coloured form 2 τ=200sec. and for coloured form 4 $\tau > 10^4$sec,(toluene,t= 20°C). In this case role of E,Z-isomerisation of form 4 may be considerable.

Other indolic fulgide synthesised from 1-ethyl-3-formyl indole did not possess heliochromic properties.On irradiation (λ=403nm.)leads to E-isomer.Revers reaction ouccured on sunlight.On boiling of the fulgide in o-dichlorbenzene using $ALCL_3$,$SnCL_4$(0.001mol.) coloured cyclic product does not form.

It is observed that the isopropylidene derivative of 1[5] was colouring on sunglight($\Delta\lambda$=95nm) during 0.2-1 min.Reverse reaction occurred in the dark during 1.5-3.0 min.These properties allow to use it as heliochromic material.

APPENDIX

2-Adamantyliden-E(1methyl-2indolylmethylen)succinic anhydride

1.6g.(0.01mol.) 1-methyl- 2-formylindole was condensed with diethyl adamantylidensuccinate 3.1g. (0.011mol.)in toluene (100cm.^{3}) using sodium hydride 0.8g.(0.03mol) as condensing agent. After saponification by the 10% ethanolic potassium hydroxide and cyclisation by the 10% ethereal acetic anhydride gave E-fulgide 1 to yield 95%,after recrystalisation from CCl_4 ,m.p. 215-216°C.

irradiation (λ=415nm) towards the ring closure reaction to form cycle product 2 (λ=534nm). Cycle product 2 of indolic fulgide undergoes a termal 1,5-H shift to form 3 which under conditions of experiment (irradiation λ=415-420nm.,toluene, t=60^{0}C) produced coloured form 4 (λ=552nm) reversibly.If we break irradiation and keep the solution in the dark during 3-4 hours, coloured product 4 transforms into cycle form 3. Heliochromic properties of compound 3 displays on sunglight irradiation during 0.5-1.5 sec., which produced reversibly red-cherry coloured form 4.The reverse reaction occurred in the dark.In ^{1}H-NMR-spectrum of coloured solution signals are observed from form 4,which can undergo E,Z-isomerisation on sunglight.By means of flash-photolysis there was determined the time of semitransformation for coloured form 2 τ=200sec. and for coloured form 4 $\tau>10^{4}$sec,(toluene,t= 20^{0}C). In this case role of E,Z-isomerisation of form 4 may be considerable.

Other indolic fulgide synthesised from 1-ethyl-3-formyl indole did not possess heliochromic properties.On irradiation (λ=403nm.)leads to E-isomer.Revers reaction ouccured on sunlight.On boiling of the fulgide in o-dichlorbenzene using $ALCL_3$,$SnCL_4$(0.001mol.) coloured cyclic product does not form.

It is observed that the isopropylidene derivative of 1[5] was colouring on sunglight($\Delta\lambda$=95nm) during 0.2-1 min.Reverse reaction occurred in the dark during 1.5-3.0 min.These properties allow to use it as heliochromic material.

APPENDIX

2-Adamantyliden-E(1methyl-2indolylmethylen)succinic anhydride

1.6g.(0.01mol.) 1-methyl- 2-formylindole was condensed with diethyl adamantylidensuccinate 3.1g. (0.011mol.)in toluene (100cm.^{3}) using sodium hydride 0.8g.(0.03mol) as condensing agent. After saponification by the 10% ethanolic potassium hydroxide and cyclisation by the 10% ethereal acetic anhydride gave E-fulgide 1 to yield 95%,after recrystalisation from CCl_4 ,m.p. 215-216^{0}C.

2-Adamantyliden-E(1ethyl-3indolylmethylen)succinic anhydride

1.72g. (0.01mol.) 1-ethyl-3-formylindole was condensed with diethyl adamantylidensuccinate 3.1g. (0.011mol.) in toluene (100cm.) using sodium hydrid 0.8g (0.03mol.) as condensing agent.After saponification by the 10% ethanolic potassium hydroxide and cyclisation by the 10% ethereal acetic anhydride gave E-fulgide 5 (λ=403nm. ,Z-isomer λ=415nm.) to yield 96% after recrystalisation from CCl_4,m.p.165-166^{o}C.

REFERENCE

1. H.G.Heller, S.N.Oliver, J.Whittal,W.Johncock,P.J. Darcy, C.Trundle (USA), Photochromic fused-ring organic compounds and their use in photoreactiv lenses, U.K.P.A.2146327A GB.

2. K.Ulrich, H.Port, H.C.Wolf, J.Wonner, F.Effenberger, H.d.Ilge,Photochromic thiofenefulgides.Photokinetics of two isopropyl derivatives.,Chemical Physics 154, 311-312,(1991)

3. Tanaka Takashi,Tanaka Kenji, Imura Satoshi, Kida Yasuji, Novel photochromic compounds,process for production thereof use thereof and composition contaning said photochromic compound, E.P.A. 0315112 (1989).

4. Tanaka Takashi, Imura Satoshi, Kida Yasuji, Photochromic compounds, E.P.A 0316179.

5 .I.Y. Grishin,,N.M. Przhiyalgovskaya,Y.M. Chunaev, V.F. Mandzhikov, L.N. Kurkovskaya, N.N. Suvorov, Photochromic fulgides on base 1-methyl-2-formylindole,Chimiya Geterocicl. Soedin. (RUSS.),1989, № 7 s.907-910.