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Birgit Künkemeier-Schröder[a]; Astrid-C. Koch[a]; Gerhard Pelzl[b]; Willy Friedrichsen[b]
[a] Institut für Organische Chemie, Universität Kiel, Kiel, Germany [b] Institut für Physikalische Chemie-Fachbereich Chemie, Martin-Luther-Universität Halle, Halle, Germany

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Pyrazolo[1, 2-a]pyrazoliumolates as novel structure elements in liquid crystals [1]

by BIRGIT KÜNKEMEIER-SCHRÖDER†, ASTRID-C. KOCH†
GERHARD PELZL‡ and WILLY FRIEDRICHSEN‡*

† Institut für Organische Chemie, Universität Kiel,
Olshausenstraße 40/60, D-24098 Kiel, Germany
‡ Institut für Physikalische Chemie—Fachbereich Chemie,
Martin-Luther-Universität Halle,
Mühlpforte 1, O-4020 Halle, Germany

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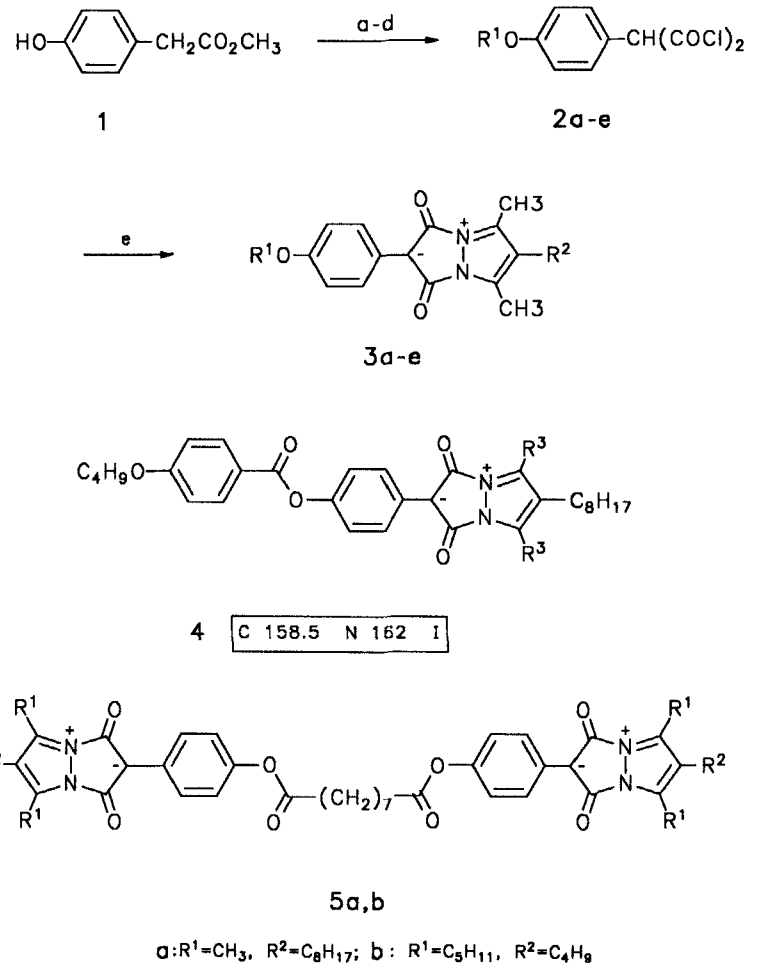
A series of pyrazolo[1, 2-a]pyrazoliumolates of type **3**, **4**, and **5** was prepared. Compound **4**($R^3 = CH_3$) shows liquid crystalline properties (C 158·5 N 162 I).

The overwhelming majority of compounds which exhibit thermotropic liquid crystal (LC) properties contain aryl and/or cycloalkyl groups [2, 3]. Heterocyclic compounds seemingly have been used to a less extent [4, 5]. In order to gain insight into the behaviour of LCs with highly dipolar structure elements [6], we tried to use cross-conjugated mesomeric betaines [7] as novel building blocks. In this paper, the first example of a pyrazolo[1,2-a]pyrazoliumolate [8, 9, 10] with LC properties is described.

At the outset of our work it was still unknown whether *two* core elements would be sufficient for LC behaviour. Therefore 2-aryl substituted betaines of type **3** were prepared as shown in the scheme. Methyl 4-hydroxyphenylacetate was *O*-alkylated, transformed to malonic acid derivatives of type **2** and finally condensed with 3-alkyl-2,4-dimethylpyrazoles [11] to give **3a–e** [12]. Optical investigations showed that these betaines do not exhibit any LC behaviour. The elongation of **3f** [13], which could be prepared from **3b** by treatment with $TiCl_4/CH_2Cl_2$, with an aromatic ester moiety proved to be successful. The esterification of **3f** with *4-n*-butoxybenzoic acid yields **4** ($R^3 = CH_3$) [14] which shows LC behaviour albeit in a narrow region: on melting at 158·5°C a nematic phase is observed [15]; at 162°C the isotropic phase appears. On cooling down the range of the nematic phase could be extended to 142°C.

2, 3	R^1	R^2	mp(**3**)/°C
a	C_6H_{13}	C_6H_{13}	111
b	$(CH_3)_2CH$	C_8H_{17}	126
c	C_6H_{13}	C_8H_{17}	115
d	C_8H_{17}	C_8H_{17}	110
e	$C_{12}H_{25}$	C_8H_{17}	102
f	H	C_8H_{17}	178
g	$C_6H_{11}CO$	C_8H_{17}	102

* Author for correspondence.



a: alkylbromide/K_2CO_3/acetone; b: $OC(OEt)_2$/Na; c: KOH/CH_3OH; d: $SOCl_2$; e: 3-alkyl-2,4-dimethylpyrazole/Et_3N (alkyl: C_6H_{13}, C_8H_{17})

The extension of these investigations to other compounds of type **3** (C_5H_{11} versus CH_3) and twins of type **5** (prepared from bismalonic acid derivatives and pyrazoles) showed that these compounds did not exhibit LC behaviour. Whether cross-conjugated mesomeric betaines and other dipolar heterocycles (as pyrimidiniumolates [16, 17]) are advantageous or detrimental for LCs remains to be explored.

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[12] All new compounds described in this communication have been fully characterized by IR, UV, ^{1}H NMR, ^{13}C NMR and high resolution mass spectrometry. For details see Supplementary Material which has been deposited in the British Library. (Copies of this material which comprises 9 pages may be obtained from the British Library, Lending Division, by quoting the number SUP 16524 according to the procedure described at the end of this issue.)

[13] **3f**: red crystals; mp 178°C (ethyl acetate-petrol ether); UV(CH_3CN) λ (lg ε) 208 (4·58), 227 (4·51), 267 (4·75), 440 (3·07); ^{1}H NMR($CDCl_3$): δ 0·9 (t, 3 H, CH_3), 1·25 (m, 12 H, CH_2), 2·3 (t, 2 H, CH_2), 2·50 (s, 6 H, CH_3), 5·15 (s, 1 H, OH), 6·8 (d, 2 H), 7·9 (d, 2 H).

[14] **4**: orange red needles; mp 158·5°C (ethyl acetate); UV(CH_3CN) λ (lg ε) 209 (4·53), 271 (4·64), 415 (2.78); ^{1}H NMR($CDCl_3$): δ 0·87 (6 H, CH_3), 1·2–1·8 (m, 16 H, CH_2), 2·33 (t, 2 H, CH_2), 2·53 (s, 6 H, CH_3), 4·03 (t, 2 H, OCH_2), 6·95 (d, 2 H), 7·15 (d, 2 H), 8·13 (2 d, 4 H).

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