

Heterocyclic derivatives of long-chain diacetylenic acids

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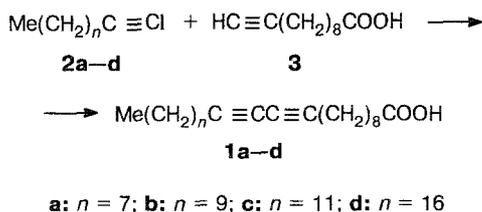
Acyl derivatives of 2-aminopyridine, 2-aminopyrimidine, 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl, and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl were obtained from long-chain diacetylenic acyl chlorides and the corresponding heterocyclic compounds. Spreading isotherms of monolayers on a water surface show that lengthening of the hydrocarbon chain and replacement of the pyridyl groups in these compounds by the more hydrophilic pyrimidyl groups render the films more condensed. Long-chain acyl derivatives of nitroxyl radicals form monolayers possessing a low collapse pressure. ESR spectra of Langmuir–Blodgett films of these radicals before and after photopolymerization were recorded.

Key words: long-chain diacetylenic acids, *N*-pyridyl and *N*-pyrimidylamides of alkanediynic acids, long-chain derivatives of nitroxyl radicals, synthesis, monolayers, Langmuir–Blodgett films.

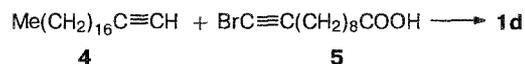
In recent years, photopolymerization of diacetylenic compounds in Langmuir–Blodgett films (LB films) was studied intensely. Alkanediynic acids,¹ whose polymers possess nonlinear optical properties,² have been studied most thoroughly in this respect. The carboxylic group in such acids does not play a decisive role in determining the properties of the resulting films, but is required, primarily, as a hydrophilic group to impart surface-active properties to the monomer. On the other hand, introduction of other chemically active terminal groups, possessing complex-forming, catalytic, or luminescent groups or having the capability to serve as electron donors or acceptors, into polymerizable diacetylenic compounds considerably affects the properties of the films and expands the potential of their application. One of the simplest methods for forming such terminal groups involves modification of the carboxyl group in long-chain acids.

In the present work we report on the synthesis of derivatives of some diacetylenic acids, including free radical derivatives, and their capability of forming monolayers and LB films.

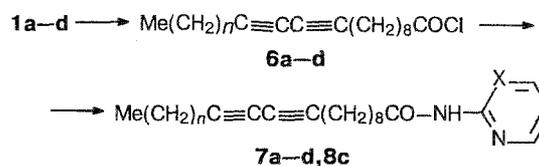
The starting diacetylenic acids **1** were obtained by coupling 1-iodo-1-alkynes with undec-10-ynoic acid (**3**) according to the Chodkiewicz–Cadiot reaction^{3,4}:



Acid **1d** was also synthesized from nonadec-1-yne (**4**) and 11-bromoundec-10-ynoic acid (**5**), but the yield of the product was much less than that in the previous method.



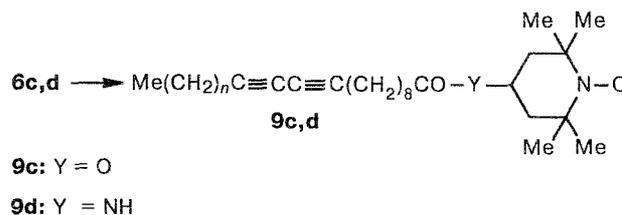
Diacetylenic acids **1** were then treated with SOCl_2 to give acyl chlorides **6**, which, without purification, were reacted with 2-aminopyridine and pyrimidine:



7a–d: X = CH

8c: X = N

Long-chain derivatives of free nitroxyl radicals **9c,d** were synthesized similarly:



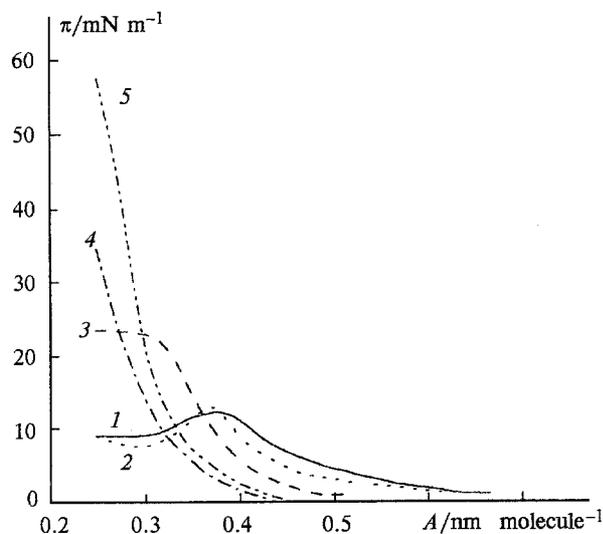


Fig. 1. Surface tension—area isotherms for heterocyclic amides **7a** (1), **7b** (2), **7c** (3), **7d** (4), and **8c** (5) at 14 °C.

The isotherms of monolayer compression for compounds **7** and **8** are presented in Fig. 1. *N*-Pyridylamides **7a** and **7b** form liquid-expanded films with low collapse pressure, in which a molecule occupies a large square in a monolayer, *i.e.*, the molecules are packed loosely in the film and form different angles with the surface. When the hydrocarbon chain length increases, packing is improved, and transition of the monolayer from the liquid-expanded to condensed state (amide **7d**) is observed. This is consistent with the previously found linear dependence of the collapse pressure on the overall length of the hydrocarbon chain in a series of di- and triacetylenic acids with the same position of multiple bonds relative to the carboxyl group.⁵ The area occupied by a molecule in a condensed monolayer of amide **7d** is $\sim 35 \text{ \AA}^2$, which almost coincides with the area of the pyridine ring. This suggests that the "molecule head", *i.e.*, the pyridine ring, lies planarly on water surface. A similar result was obtained for 4-(octadec-17-enyl)pyridine.⁶ Unlike pyridylamide **7c**, its pyrimidine analog forms a condensed monolayer, probably because of an increased hydrophilicity of the "head" group due to its second nitrogen atom (see Fig. 1).

Nitroxyl radicals **9** have a bulky and weakly hydrophilic head group, which should prevent the molecules from common orientation and hinder dense packing of molecules in the monolayer. However, the molecules of radical **9c** in a compressed monolayer are likely to be arranged rather regularly, although the collapse pressure is not high (Fig. 2). Although radical **9d** has a long hydrocarbon chain, it forms a typical liquid-expanded film on a water surface (see Fig. 2). This is probably explained by the presence of an amide group, which can form an intermolecular bond with the radical center.

To our knowledge, LB films based on polymerizable long-chain derivatives of stable radicals have not been

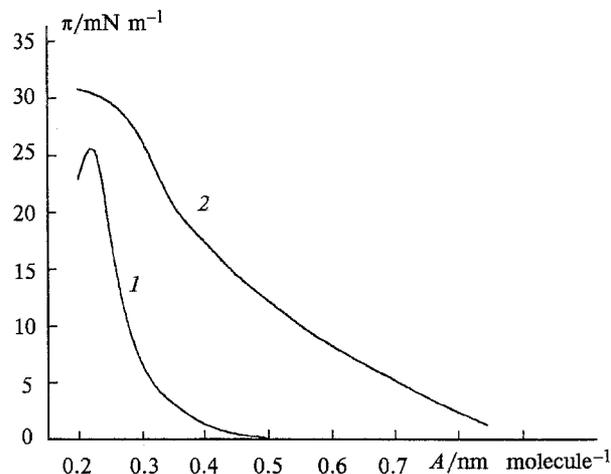


Fig. 2. Surface tension—area isotherms for free radicals **9c** (1) and **9d** (2) at 17 °C.

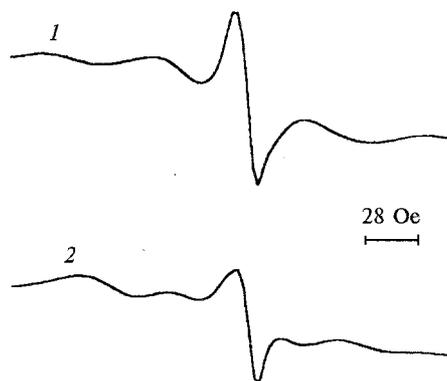


Fig. 3. ESR spectra of an LB film of radical **9c** before (1) and after (2) photopolymerization.

reported so far. We obtained mixed films of compounds **9c,d** containing 33.5 mol.% methyl behenate, with a thickness of up to 50 monolayers. Figure 3 presents the ESR spectra of such a film obtained from radical **9d** before and after polymerization by UV light. In both cases, signal broadening is much stronger than that in the spectrum of crystalline monomer **9c**. The ESR spectrum of radical **9d** in a film before polymerization is almost the same as that of radical **9c**, but photolysis results in complete disappearance of the signal. The characteristic change in film color⁵ does not occur, and the film only becomes slightly pink. We relate these anomalies to the weak ordering of molecules **9d** in the film, which results in formation of separate restricted conjugation sites and leads to involvement of the radical center of the monomer in the reaction.

Experimental

IR spectra of the compounds obtained were recorded on a UR-20 spectrophotometer in CHCl_3 in NaCl cells. ^1H NMR

Table 1. Characteristics of diacetylenic compounds

Compound	Yield (%)	M.p./°C (solvent)	Found/Calculated (%)			Molecular formula
			C	H	N	
1a	47	55–56 (pentane)	<u>78.91</u> 79.19	<u>10.55</u> 10.76		C ₂₁ H ₃₄ O ₂
1b	48	58–59 ¹² (pentane)	—	—		C ₂₃ H ₃₈ O ₂
1c	52	61–62 ¹³ (hexane)	<u>80.15</u> 80.16	<u>11.38</u> 11.30		C ₂₅ H ₄₂ O ₂
1d	61	72–74 (hexane)	<u>81.06</u> 81.02	<u>11.73</u> 11.79		C ₃₀ H ₅₂ O ₂
7a	60	46–47 (hexane)	<u>78.94</u> 79.14	<u>9.63</u> 9.71	<u>6.98</u> 7.10	C ₂₆ H ₃₈ N ₂ O
7b	66	52.5–53 (pentane)	<u>79.41</u> 79.57	<u>9.83</u> 10.02	<u>6.55</u> 6.63	C ₂₈ H ₄₂ N ₂ O
7c	67	58.5–59 (hexane)	<u>79.92</u> 79.95	<u>10.16</u> 10.29	<u>6.36</u> 6.22	C ₃₀ H ₄₆ N ₂ O
7d	61	70–71 (hexane)	<u>80.44</u> 80.71	<u>10.76</u> 10.84	<u>5.37</u> 5.38	C ₃₅ H ₅₆ N ₂ O
8c	65	75–76 (methanol)	<u>77.11</u> 77.11	<u>10.16</u> 10.04	<u>9.49</u> 9.30	C ₂₉ H ₄₅ N ₃ O
9c^a	61	37–37.5 (methanol)	<u>77.08</u> 77.21	<u>10.89</u> 11.05	<u>2.71</u> 2.66	C ₃₄ H ₅₈ NO ₃
9d^b	38	42–43 (ether)	<u>77.92</u> 78.47	<u>11.43</u> 11.48	<u>4.56</u> 4.69	C ₃₉ H ₆₉ N ₂ O ₂

^a Found: 6.07 · 10²³ spins mol⁻¹ (reference: CuCl₂ · 2H₂O). ^b Found: 6.11 · 10²³ spins mol⁻¹.

spectra were obtained on a JEOL FX90Q spectrometer (90 MHz) in CDCl₃ relative to SiMe₄. ESR spectra were obtained on a Bruker ESP-300 radio-frequency spectrometer. Terminal acetylenes were obtained by alkylation of NaC≡CH with alkyl bromides in DMF (see Ref. 7), while their 1-iodo derivatives **2a–d** were synthesized from copper acetylenides and I₂ by a known procedure.⁸ The free radicals, 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (m.p. 70–71 °C) and 4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl (m.p. 33.5–35 °C), were synthesized by a known procedure.⁹ Bromide **5** was obtained by a published procedure,¹⁰ and acetylene **3** by a known procedure in Ref. 11. The physicochemical characteristics of all of the diacetylenic compounds synthesized in this work are presented in Tables 1 and 2.

To form a monolayer, the corresponding compound was dissolved in a hexane–CHCl₃ mixture and placed onto the surface of deionized water filtered through 0.2 μm membranes. The conditions for obtaining monolayers and LB films have been reported previously.⁵ The LB films of nitroxyl radicals were obtained from their mixtures with methyl behenate (molar ratio radical : ester, 2 : 1). The LB films of radical **9c**, 50 monolayers in thickness, deposited on a glass support at a pressure of 0.24 mN m⁻¹, were studied. A high-pressure mercury lamp was used for irradiation.¹³

Triacenta-10,12-diyinic acid (1d). A. Bromide **5** (1.31 g, 5 mmol) in MeOH (10 mL) and a 25% solution of MeNH₂ (3 mL) were gradually added¹⁰ over a period of 30 min in a stream of N₂ to a mixture of alkane **4** (1.32 g, 5 mmol), CuCl (125 mg, 1.25 mmol), and a 25% solution of MeNH₂ (5 mL) in MeOH–THF (1 : 1, 25 mL) decolorized by a small amount of NH₂OH · HCl. The mixture was stirred for 2 h at 20 °C

Table 2. Spectral characteristics of diacetylenic compounds

Compound	¹ H NMR, δ (J/Hz)	IR spectrum, ν/cm ⁻¹
1a	0.88 (t, 3 H, CH ₃ , <i>J</i> = 7); 1.3 (s, 24 H, CH ₂); 2.2–2.4 (m, 6 H, CH ₂ C=O and CH ₂ C≡C)	1720 (C=O)
7a	0.88 (t, 3 H, CH ₃ , <i>J</i> = 7); 1.26 (s, 24 H, CH ₂); 2.1–2.5 (m, 6 H, CH ₂ C≡C and CH ₂ C=O); 6.9–7.1 (m, 1 H, H(5)); 7.67 (t d, 1 H, H(3), <i>J</i> _{3,4} = 7.1, <i>J</i> _{3,5} = 2.7); 7.95 (s, 1 H, NH); 8.1–8.3 (m, 2 H, H(4), H(6))	1520 (NH) 1695 (C=O) 3440 (NH)
8c	0.89 (t, 3 H, CH ₃ , <i>J</i> = 7); 1.29 (s, 32 H, CH ₂); 2.26 (t, 4 H, <i>J</i> = 7.5, CH ₂ C≡C); 2.75 (t, 2 H, <i>J</i> = 8, CH ₂ C=O); 7.0 (t, 1 H, H(4), <i>J</i> = 6.8); 8.4 (s, 1 H, NH); 8.6 (d, <i>J</i> = 6.8, 2 H, H(3) and H(5))	1590 (NH) 1690 (C=O) 3400 and 3440 (NH)
9c	–20 ÷ –60 (s, CH, CH ₂ and CH ₃ in the cycle), 0.8–1.0 (s, CH ₃ in the chain), 1.2–1.5 (s, CH ₂ in the chain), 2.1–2.4 (s, CH ₂ C≡C and CH ₂ C=O)	1720 (C=O)

Note. The signal positions in the ¹H NMR spectra of compounds **1b–d** almost coincide with the data for compounds **1a**, **7b–d** with **7a**; **9d** with **9c**. All signals in the ¹H NMR spectra of compounds **9c** and **9d** are broadened.

and for 1 h at 40 °C, acidified by HCl with cooling, and extracted with ether. The extract was dried with MgSO₄, and the solvent was removed. The residue was dissolved in hexane, filtered through a thin layer of Woelm polyamide, and recrystallized three times from hexane to give 0.86 g of diyne **1d** as white crystals that turned blue in air.

B. Compound **2d** (7.80 g, 20 mmol) in THF (40 mL) was added over a period of 2 h in an N₂ atmosphere to a solution of compound **3** (3.64 g, 20 mmol),¹¹ KOH (4 M, 5 mL), CuCl (0.50 g, 5 mmol), and 25 % aqueous MeNH₂ in a MeOH—THF mixture (80 mL, 1 : 1) decolorized by a small amount of NH₂OH·HCl. The mixture was stirred for 4 h at the same temperature and for 1 h at 40 °C. Compound **1d** (5.4 g) was obtained.

Acids **1a—c** were synthesized by method **B** in MeOH.

Triacenta-10,12-diyneoyl N-(2-pyridyl)amide (7d). A mixture of compound **1d** (0.44 g, 1 mmol), SOCl₂ (0.60 g, 5 mmol), and DMF (20 μL) in pentane (50 mL) was refluxed until gas evolution ceased. The mixture was stirred for an additional 1 h at the same temperature and filtered. The solvent was removed *in vacuo*. The resulting crude **6d** (0.46 g, ~100 %, m.p. ~30 °C) and 2-aminopyridine (0.30 g, 3.2 mmol) were stirred in dry benzene (15 mL) for 3 h at 20 °C and for 1 h at 60 °C. Water (20 mL) was added, and the organic layer was separated and additionally washed several times with water. The benzene was distilled off *in vacuo*. The residue was dissolved in an ether—pentane mixture (10 mL, 1 : 1) and filtered through a small layer of SiO₂. Compound **7d** (white crystals) that precipitated on cooling was separated, yield 0.46 g.

Compounds **7a—c** were obtained in a similar way.

Pentacosa-10,12-diyneoyl N-(2-pyrimidyl)amide (8c). Crude compound **6c** (obtained from **1c** (0.50 g, 1.34 mmol) and 2-aminopyrimidine (0.14 g, 1.5 mmol)) was stirred for 2 h in dry benzene (1.5 mL) and pyridine (2 mL) on a boiling water bath, diluted with benzene (20 mL), and washed with water. After drying with K₂CO₃, the solvent was cautiously (foaming!) distilled off *in vacuo*. The residue was dissolved in CHCl₃, filtered through SiO₂, and crystallized from MeOH to give 0.39 g of compound **8c**.

4-(Pentakosa-10,12-diyneoxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (9c). 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (0.146 g, 0.85 mmol) and Et₃N (4 mL) in dry ether (30 mL) was mixed at 0 °C with compound **6c** and stirred for 30 min at 20 °C. The Et₃NH⁺Cl⁻ that precipitated was filtered off, and the solvent was removed *in vacuo*. Pentane (20 mL) was added to the residue; the mixture was filtered, and the solvent was distilled off. Crystallization from MeOH gave 0.100 g of product **9c**; preparative TLC of the mother liquor gave an additional 0.090 g of **9c**.

4-(Triacenta-10,12-diyneoylamino)-2,2,6,6-tetramethylpiperidine-1-oxyl (9d). Compound **6d** (0.155 g, 0.33 mmol) in benzene (25 mL) was added dropwise at ~6 °C to a mixture of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (0.040 g, 0.23 mmol) and Et₃N (0.5 mL) in dry benzene (25 mL). The mixture was stirred for 2 h at 20 °C and filtered. The solvent was distilled off *in vacuo*. Thin layer chromatography on SiO₂ and crystallization from ether gave 90 mg of compound **9d**.

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