

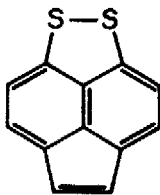
PERI-BRIDGED NAPHTHALENES. 4. CHALCOGEN-BRIDGED ACENAPHTHYLENES

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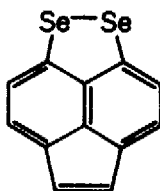
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Abstract: Three new electron donors, acenaphtho[5,6-cd]-1,2-dithiole (1), acenaphtho[5,6-cd]-1,2-diselenole (2), and acenaphtho[5,6-cd]-1,2-ditellurole (3), can be prepared in 28%, 22%, and 14% yields respectively by reaction of the elemental chalcogens (S, Se, Te) with 5,6-dilithioacenaphthylene (4). Compound 4 is generated by treatment of 5,6-dibromoacenaphthylene (5), for which a convenient preparation is described, with *n*-butyllithium (2 equiv.) in THF at -78°C.

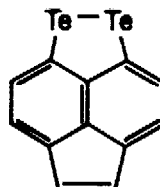
Charge transfer complexes derived from organic π -electron donors and electron acceptors continue to attract the attention of chemists and physicists interested in the electrical properties of solids.¹ We have recently described the synthesis and properties of complexes derived from some novel donor molecules, naphthalene dichalcogenides,² and we now report the synthesis of the acenaphthylene analogs (1-3) of these chalcogen-bridged naphthalenes.



1

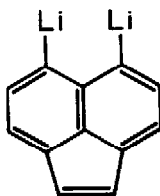


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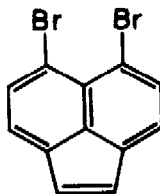


3

In analogy to our earlier work, our approach to the desired sulfur, selenium and tellurium bridged acenaphthylenes required 5,6-dilithioacenaphthylene (4) as a key intermediate. This intermediate should be available via metal-halogen exchange from 5,6-dibromoacenaphthylene (5) and an alkyl lithium. A practical source of 5, therefore, became our first objective. (While 5 is a known compound, the previously reported syntheses are lengthy and inefficient.)³

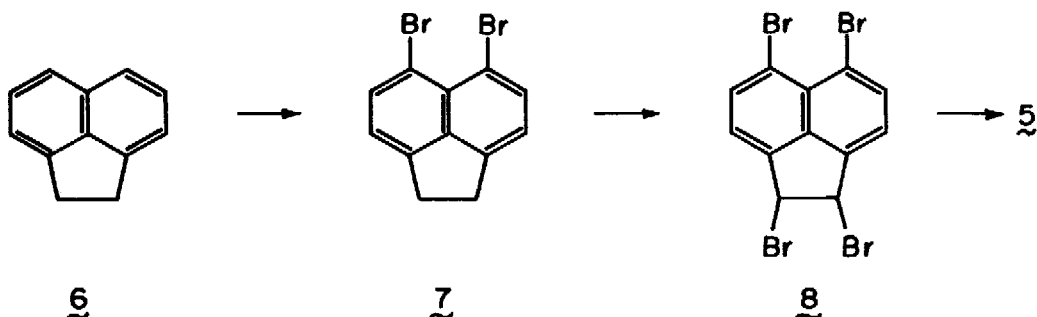


4



5

We have developed a convenient preparation of **5**, starting from acenaphthene (**6**), which is outlined below. The bromination of **6** with *N*-bromosuccinimide (2 equiv.) in propylene carbonate, below 25°C, give 5,6-dibromoacenaphthene (**7**)⁴ directly in 25% yield. Further bromination of **7** with *N*-bromosuccinimide [2 equiv., CCl₄, (C₆H₅CO₂)₂] gives **8**³ (84%, *cis*, *trans* mixture), which is readily debrominated to **5** (73% yield) upon treatment with zinc dust in ethanol.



The desired 5,6-dithioacenaphthylene (**4**) was generated from **5** by treatment with *n*-butyllithium (2 equiv.) in THF at -78°C. For the synthesis of **1**, elemental sulfur was introduced (-78°C) and the reaction quenched by addition of a 25% solution of glacial acetic acid in THF as soon as the sulfur had dissolved. The reaction mixture was then warmed to room temperature and exposed to air for one hour. Chromatography of the resulting red solution on Florisil, using hexane as eluent, gave an orange band of acenaphtho[5,6-*cd*]-1,2-dithiole (**1**) which was obtained as red-orange crystals in 28% yield after sublimation (90°C, 0.03 mm Hg). Thermal gradient sublimation at 110°C gave a pure sample of **1** as red crystals, m.p. 180-182°C; Anal. calcd. for C₁₂H₆S₂: C, 69.29; H, 2.80. Found: C, 69.05; H, 2.98. ¹H-NMR (CDCl₃): δ 7.29 (s, 2H), 7.59 (d, 2H, J = 8.2 Hz), 7.93 (d, 2H, J = 8.2 Hz). ¹³C-NMR (CDCl₃): 143.4, 132.9, 130.7, 128.6, 125.6, 125.4, and 115.9 ppm.

The analogous procedure, substituting elemental selenium for sulfur, gave acenaphtho[5,6-*cd*]-1,2-diselenol (**2**) in 22% yield. After vacuum sublimation and thermal gradient sublimation, **2** was obtained as black needles, m.p. 170-171°C; Anal. calcd. for C₁₂H₆Se₂: C, 46.77; H, 1.95. Found: C, 46.61; H, 2.03. ¹H-NMR (CDCl₃): δ 7.20 (s, 2H), 7.67 (d, 2H, J = 7.8 Hz), 7.80 (d, 2H, J = 7.8 Hz). ¹³C-NMR (CDCl₃): 135.0, 126.6, 125.8, 125.3, 121.5, 121.0, and 120.8 ppm.

In the case of the reaction of **4** with tellurium, it proved necessary to use fresh, finely divided tellurium, and to carry out the reaction at a somewhat elevated temperature (-30°C). Since **3** itself was less stable than its lower molecular weight analogs, both reaction and isolation times were minimized. Under our best conditions, acenaphtho[5,6-*cd*]-1,2-ditellurole (**3**) was isolated as brownish-black needles, m.p. > 350°C (dec.), in 14% yield after sublimation (120°C, 0.03 mm Hg). Anal. calcd. for C₁₂H₆Te₂: C, 35.54; H, 1.48. Found: C, 36.11; H, 1.75. ¹H-NMR (FT, acetone-*d*₆): δ 7.10 (s, 2H), 7.68 (d, 2H, J = 7.2 Hz), 7.99 (d, 2H, J = 7.2 Hz).

Observation of the molecular ion clusters in the 70 eV EI mass spectra of **1-3**, and comparison of the recorded spectra with calculations based on the natural isotopic abundances of S, Se, and Te (see Table 1) provided excellent support for the composition of these acenaphthylene derivatives.

Black TCNQ complexes of 1-3 were prepared using 1 equiv. of TCNQ in acetone. The room temperature resistivity of 1 and 2, using a compressed pellet, gave values of 10^8 and 10^7 Ohm cm, respectively. The TCNQ complex of 3 was unstable at room temperature, and gave a less accurate resistivity measurement ($\sim 2 \times 10^4$ Ohm cm). Comparing these results with those obtained for the TCNQ complexes of the previously described chalcogen bridged naphthalenes,² we find that the sulfur and selenium compounds in each series show resistivities of the same magnitude. Because of the instability of the complex derived from 3, however, no conclusion about the corresponding tellurium compounds can be reached.

Table 1: Molecular Ion Clusters of Chalcogen-Bridged Acenaphthylenes

1		2		3	
m/e	intensity #	m/e	intensity	m/e	intensity
214	100(100)	302	4(4)	397	2(2)
215	15(15)	303	6(5)	398	6(6)
216	9(10)	304	20(20)	399	5(5)
217	1(1)	305	15(15)	400	17(17)
		306	51(52)	401	16(15)
		307	34(32)	402	37(36)
		308	87(89)	403	26(26)
		309	19(16)	404	66(67)
		310	100(100)	405	27(29)
		311	15(13)	406	100(100)
		312	35(40)	407	13(13)
		313	5(4)	408	94(93)
		314	5(3)	409	12(12)
				410	50(51)
				411	6(7)

intensity observed (calculated).

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