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FULVALENE TYPE COMPOUNDS CONTAINING 1,3-DITHIEPIN COUNTERPART. QUALITATIVE EVALUATION OF THE ELECTRON ACCEPTING ABILITY OF 1,3-DITHIEPIN SYSTEM

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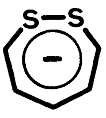
Some fulvalenoids containing 1,3-dithiepin counterpart (**5a**), (**5b**), and (**5c**) have been synthesized through the reaction of 2-trimethylsilyl-1,3-dithiepinide ion (**6**) with di-*tert*-butyl-cyclopropenone, 2,3;6,7-dibenzotropone, and fluorenone, respectively. Comparison of the ^{1}H-NMR spectra of these fulvalenes indicated the electron accepting ability of the 1,3-dithiepin moiety.

Recently the theoretical1) as well as the experimental attentions have been paid to the elucidation of the aromaticity of the three potentially aromatic dithiepinyl anions (**1**), (**2**), and (**3**). Recent publications by us2) and Grohmann et al.3) indicate that the 1,4-dithiepinyl anion (**3**) does not seem to exhibit any aromatic stability associated with cyclic 10π electron system. However, in sharp contrast to **3**, the 1,3-dithiepinyl anion (**2**) has been characterized as a potentially 10π-heteroaromatic system although the degree of aromaticity seems to be small.4,5) In view of these precedents, the fulvalene type compounds (**4**) consisting of a 1,3-dithiepin and a cyclic conjugated counterparts with odd-number of n are expected to show dipolar character whereas the molecules (**4**) having even-number of n are not. We now wish to present the synthesis and some structural features of **5a**, **5b**, and **5c**.



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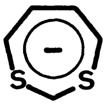

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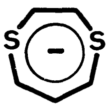

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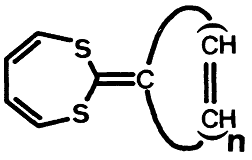

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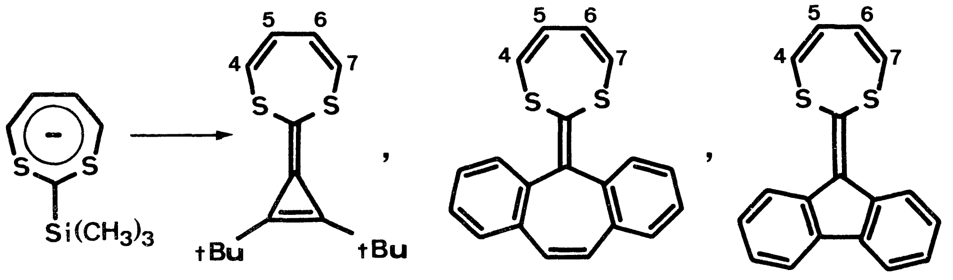
The synthesis of the model compounds of 4, such as 5a, 5b, and 5c, is shown in the Scheme.

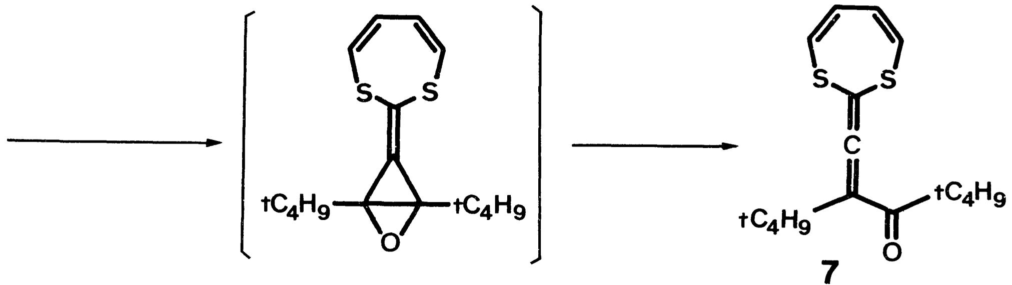


6 5a 5b 5c

2-Trimethylsilyl-1,3-dithiepinide ion (6), obtained through the sequence of reactions reported in the literature,[4,6] was treated with di-*tert*-butylcyclopropenone[8] at -70°C for 1 h to give 5a, pale yellow prisms, mp 120-122°C (from O_2 free ethanol), UV λ_{max} (CH_2Cl_2) 234 nm (log ε 4.41), 308 sh (3.85), 354 sh (3.77), in almost quantitative yield. Quite similarly, 5b, yellow prisms, mp 112-114°C (from benzene and hexane), 65% yield, UV λ_{max} (CH_2Cl_2) 287 nm (log ε 4.56) and long tailing up to 400 nm, and 5c, yellow prisms, mp 134-136°C (from benzene and hexane), 62% yield, UV λ_{max} (CH_2Cl_2) 244 nm (log ε 4.24), 259 (4.05), 335 (3.70), 377 (3.75), and long tailing up to 550 nm, were obtained through the reaction of (6) with 1,2;5,6-dibenzotropone[9] and fluorenone, respectively.

The compound 5a is thermally quite stable, however, like 5,6-dimethyl-1,2,3,4-tetraphenylcalicene[10] and 5,6-dimethyl-1,2;3,4-dibenzocalicene,[11] reacts rapidly with oxygen, giving the new compound whose structure is proved as an allenic ketone (7) by mass (m/e 294 (M^+)), ^{1}H-NMR (δ 1.16 (s, 18H), 6.25 (s, 4H)), and IR spectra ($\nu_{C=O}$ 1672 cm^{-1}, $\nu_{C=C=C}$ 1920 cm^{-1}).

5a



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In the ^{1}H-NMR spectra, most characteristic feature of 5a, 5b, and 5c can be seen in the signals of the four vinylic protons. As already reported 2H-1,3-dithiepin (8) shows the very narrow AA'BB' signals (centered at δ=6.31) for the vinylic protons whereas the same protons in the anion (9) reveals a well-separated

AA'XX' pattern ($H_{5,6}$=5.80, $H_{4,7}$=6.63, $\Delta\delta$=0.83 ppm).4) The substantial upfield shift of H-5,6 of 9 compared to those of 8 has been attributed to the considerable charge density at these positions in 9. Therefore, it might reasonably be considered that the degree of the chemical shift difference between H-4,7 and H-5,6 reflects the anionic character of the 1,3-dithiepin moiety of 5. The observed spectral pattern for the vinylic protons of 5a, 5b, and 5c are illustrated in Figure 1 and summarized in Table 1. While the fulvalene containing a three-membered ring 5a shows a moderately separated AA'BB' signals, 5c exhibits an extremely narrow doublet accompanied by small satelites. It is clear that the chemical shift difference, $\Delta\delta=\delta_{4,7}-\delta_{5,6}$, increases in order of (5c)<(5b)<(5a)<(9), parallel for the electron donating ability of the carbocyclic counterparts.12) Thus, the 1,3-dithiepin ring in 5a will tend to stabilize the dipolar form by assisting delocalization of the negative charge. The same is true to a certain extent for 5b.13)

Figure 1

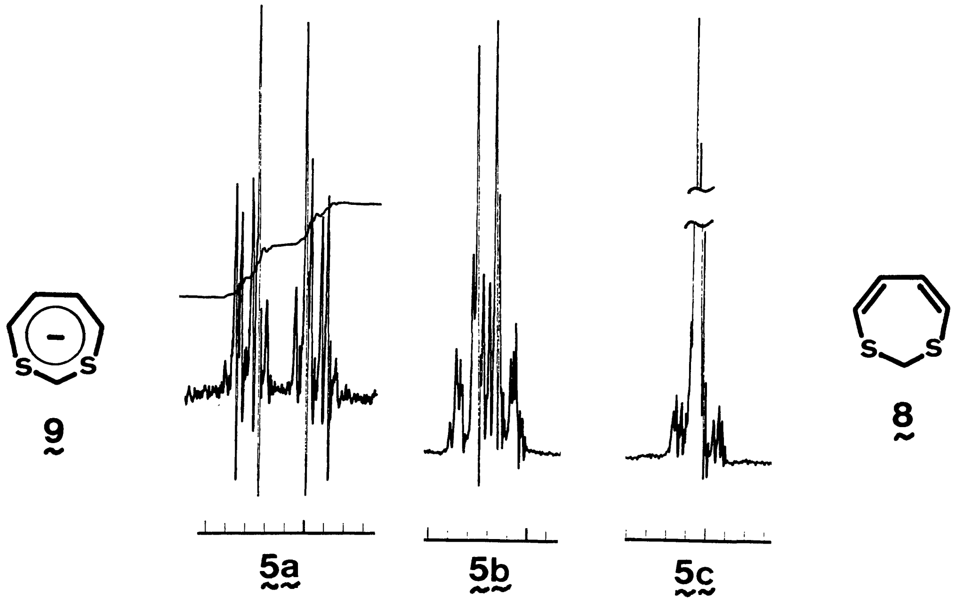

Table 1.

$\delta_{5,6}$	:	$5.80^{a)}$		$5.96^{a)}$		$6.14^{b)}$		$6.52^{b)}$		$6.29^{b)c)}$
$\delta_{4,7}$	:	6.63		6.32		6.27		6.57		$6.33^{c)}$
$\Delta\delta$	:	0.83	>	0.36	>	0.13	>	0.05	∿	0.04

a) The chemical shifts were obtained by AA'XX'-analysis. b) The chemical shifts were approximated by the center of gravity of the inner and outer multiplets. c) The H-4,7 and 5,6 assignments could be exchanged.

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References and Notes

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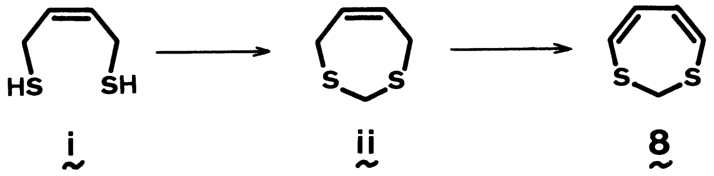
(6) Although 1,3-dithia-5-cycloheptene (**ii**)[7] and 2H-1,3-dithiepin (**8**)[4] have been synthesized by Lüttringhaus and Grohmann, respectively, these methods were slightly modified for the large scale preparation. Thus, the cycloalkylation of cis-2-butene-1,4-dithiol (**i**) with dimethoxymethane in the presence of boron trifluoride gave (**ii**) in 37% yield. In contrast to the literature[4] chlorination of (**ii**) with N-chlorosuccinimide in dry benzene, without treatment with potassium t-butoxide, afforded directly, after usual workup followed by bulb-to-bulb distillation, 2H-1,3-dithiepin (**8**) as colorless plates, bp. 50°C/0.2 Torr., mp. 28.5-30.5°C (Lit. bp. 30°C/0.05 Torr., mp. 2-4°C), in 32% yield.



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(12) Due to the diamagnetic anisotropy caused by the aromatic rings in **5b** and **5c**, it is relevant to compare the carbon chemical shifts rather than the proton chemical shifts for the present purpose. However, since heavily overlapping signals of C-4,5,6,7 with those of the aromatic carbons make it impossible to assign the carbon signals being considered, proton chemical shifts were used for convenience.

(13) Our attempts to examine the protonated species of **5a**, **5b**, **5c** in trifluoroacetic acid have so far not met with success, they led to the complex decomposition products.

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