Tetrahedron Letters No. 16, pp 1251 - 1254, 1976. Pergamon Press. Printed in Great Britain.

1,3-DITHIA-4,6-CYCLOHEPTADIENE AND ITS ANION

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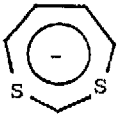
(Received in USA 6 February 1976; received in UK for publication 11 March 1976)

The experimental verification of Hückel's Rule has been an exciting chapter in organic chemistry, leading to an ever increasing number of cyclic systems classified either as aromatic or antiaromatic depending whether they obey Hückel's Rule or not. Formal replacement of a double bond unit in an aromatic molecule by a bivalent sulfur atom should cause only a minor perturbation of the $(4n+2)\pi$ - system, leading to an isoelectronic heteroaromatic system.$^{1)}$ In this way, one can derive the three potentially aromatic dithiepinyl anions (1), (2), and (3) from the cyclononatetraene anion. Theoretical calculations predict a certain ground state stabilization for the three anions (1), (2), and (3).$^{2;3)}$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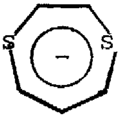
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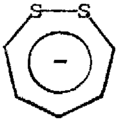
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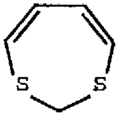
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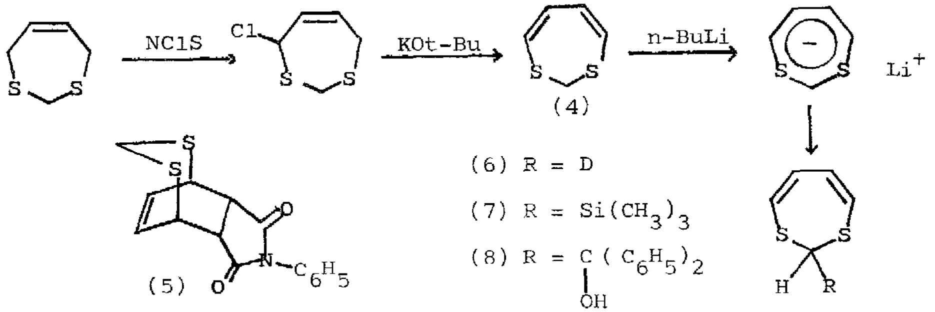
From a detailed comparison of the acidity of 2-carbomethoxydibenzo[d,f][1,3]-dithiepin with suitable model compounds, Breslow and Mohacsi concluded that there is no detectable aromaticity associated with this particular substituted derivative of (1).$^{3)}$ Furthermore, our own results as well as a recent report by Murata indicate that the 1,4-dithiepinyl anion (2) does not seem to exhibit any unusual (aromatic) stability.$^{4)}$

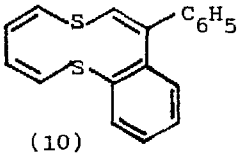
In this communication, we wish to report the synthesis of the 2-H-1,3-dithiepin (4), and the characterization of its anion (1). The known 1,3-dithia-5-cycloheptene$^{5)}$ obtained by cycloalkylation of the disodium salt of cis-2-butene-1,4-dithiol$^{6)}$ with dibromomethane in methanol , was chlorinated with N-chlorosuccinimide in dry benzene to give the very unstable 4-chloro-1,3-dithia-5-cycloheptene, which without isolation was treated with potassium t-butoxide in dry ether at 5° under Argon to give the desired diene (4) in 30 - 40 % yield as a colorless oil; bp.$_{0.05}$ 30°; mp 2 - 4°. High resolution mass spectrum: calc. $C_5H_6S_2 = 129.9911$; found 129.9903;

M^+ 130, 40 %; base peak, M - 46 = m/e 84 (loss of $CH_2=S$). After that fragmentation the mass spectrum of (4) closely resembles that of thiophene.[7] ^1H nmr($CDCl_3$): AA'BB' system δ 6.28, 4 H; singlet δ 4.13, 2 H; ^{13}C nmr[10]: 39.7 ppm (C_2), 124.7 ppm (C_5/C_6) , 128.3 ppm (C_4/C_7); uv, λ_{max}^{EtOH} 257 nm (ε 4010), λ_{max} 340nm (ε 3310). Upon heating with N-phenylmaleimide to 140° for 16 hr,(4) could be converted into its Diels Alder Adduct (5), mp 196 - 198°, which was completely characterized.



Reaction of (4) with n-butyllithium in tetrahydrofuran under Argon at -40° produced a *deep red* solution of the anion (1), which was quenched with D_2O, trimethylsilyl chloride and benzophenone to give respectively: 2-deutero-1,3-dithia-4,6-cycloheptadiene (6); (M^+ 131, base peak M - 47 = m/e 84, loss of CHD=S ; nmr: H_2 at δ 4.12, 1:1:1 - triplet); 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene (7): $bp_{0.05}$ 40 - 45°; (M^+ 202, base peak M - 73 - 32 = m/e 97, $C_5H_5S^+$ [7]); and diphenyl-2-(1,3-dithiepinyl)carbinol (8). Acid catalyzed dehydration of the carbinol (8)[8] did *not* give the expected ketene thioacetal (9) but instead an isomeric compound (10), to which we assign the ringenlarged structure of 2,3-benzo-4-phenyl-1,6-dithiacyclodecatetraene (10) based on a mechanistically similar case reported by H. Wasserman[9] and the following data: M^+ 294, 100 % ; ^1H nmr: δ 6.75, s, 1 H; δ 7.21, broad s, 5 H; δ 7.4 m, 4 H; δ 6.85 - 7.5 m, ca. 4 H; ^{13}C nmr ($CDCl_3$): fourteen different sp^2- carbon signals out of the expected sixteen.[10] The authentic ketene thioacetal (9) was obtained through the reaction of the anion derived from (7) with benzophenone.[11] Compound (9) formed yellow crystals, mp 88 - 89°, M^+ 294, 100 % ; ^1H nmr ($CDCl_3$) : δ 6.35 , AA'BB', 4 H, δ 7.26, s, 10 H; ^{13}C nmr ($CDCl_3$): eight sp^2- carbon signals, three of them quarternary.[10] The uv spectrum of (9) showed *no* distinct maxima, but a broad tailing absorption into the visible region. Saturated diphenylketene thioacetals have two distinct maxima with λ_{max} 259 nm and λ_{max} 303 nm and a shoulder at ca. 230 nm.[14]

In order to obtain some information concerning the possible presence of an induced diamagnetic ring current in (1) as a criterion for its aromaticity, we measured the proton nmr spectrum of (1) in tetrahydrofuran - d_8. (Fig. 1) Two features are very remarkable. Compared with the very narrow AA'BB'-system for the vinylic protons in (4), the same protons in the anion (1) form a well separated AA'XX'-system. Furthermore the signal for H_2 appears at δ 1.48 (t, J = 0.8 Hz).



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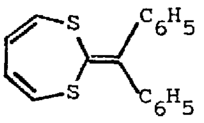

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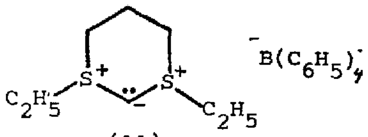

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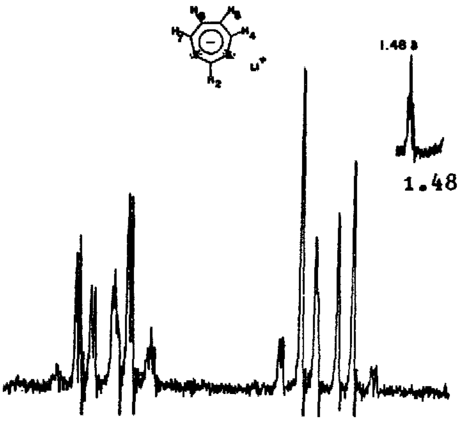

AA'XX'-Analysis for I

δ $H_{4/7}$	6.63	ppm
δ $H_{5/6}$	5.80	ppm
$J_{4,5}$	11.08	Hz
$J_{5,6}$	8.33	Hz
$J_{4,6}$	0.78	Hz
$J_{4,7}$	0.78	Hz

Diene 4

Figure 1

The assignments are based on the observation, that the signals for H_4/H_7, the low field part of the AA'XX'-system, show a fine splitting of 0.8 Hz for each line. The same W - coupling [12)] can be seen in the signal for H_2 (δ 1.48, t, $J_{2,4}=J_{2,7}=$ 0.8 Hz). In the anion (1), H_4 and H_7 are shifted <u>downfield</u> by 0.44 ppm relative to the diene (4). H_5 and H_6 are shifted <u>upfield</u> by 0.52 ppm in the anion (1) as compared to the diene (4). This indicates considerable charge density at those positions, which has to be transmitted through the sulfur. The observed W - coupling indicates a quite planar structure for the anion (1). While the chemical shift data for the vinylic protons in (1) suggest a certain delocalization of the negative charge, the chemical shift for H_2 is most puzzling. This value is substantially higher (ca. 1.00 ppm) than observed for H_2 in the related 2-lithio-1,3-dithianes[13] and the 2-lithio-bisvinylmercaptomethane.[14)] Even the ylid-salt (11) reported by Gosselck shows a higher chemical shift for H_2 than the lithiodithianes despite the positive charges at the sulfurs in (11).[15)] (Table 1) A possible interpretation of these data, although speculative at the moment, is that in the lithiodithianes we observe tetrahedral carbanions (ion pairs), stabilized through polarization at the sulfur atoms.[16)] Anion (1) and similarly ylid-salt (11) represent planar delocalized systems (10 π - aromatic delocalization in (1), and possibly d - orbital acceptance in (11)), with completely different anisotropy effects of the sulfur atoms on proton H_2. Further work is in progress in order to substantiate this more accurately.

Table 1: ^{1}H NMR Chemical Shift Data

Compound	δ H_2	Anions	δ H_2	δ H_2 – δ H_2(Anion)
1,3 Dithiane*	3.68	2-Li deriv.	2.78	0.90
cis-4,6-dimethyl-1,3-dithiane*	4.03_a; 3.40_e	2-Li deriv.	2.58_a	1.45_a; 0.82_e
Bisvinylmercaptomethane**	3.92	2-Li-deriv.	2.50	1.42
1,3-Diethylbisdithianium salt***	5.35	ylid-salt (11)	1.97	3.38
1,3-Dithia-4,6-cycloheptadiene (2)	4.13	anion (1)	1.48	2.65

*THF-d_8; E. Eliel, Personal Comm.; **THF-d_8; K. Grohmann, unpublished results; ***DMSO-d_6; counter ion $B(C_6H_5)_4^-$ see ref. 15)

Acknowledgements: We gratefully acknowledge partial support of this work by the Research Foundation of the City University of New York (FRAP Awards # 01769 N and # 10190).

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