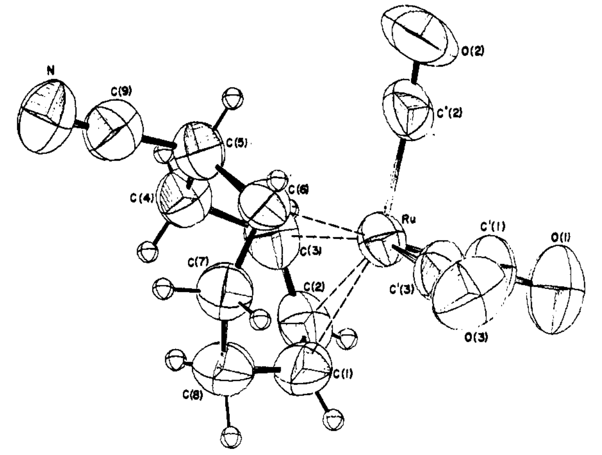


Figure 1. A perspective view of the 1,2,3,6-*tetrahapto*(5-cyanocyclooctadienyl)tricarbonylruthenium molecule.

it seems likely that most of them will behave in the same way.[4]

[4] We are grateful to the National Science Foundation and the Science Research Council (U. K.) for partial support of this work.

F. A. Cotton,* M. D. LaPrade
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

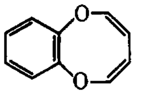
B. F. G. Johnson, J. Lewis
University Chemical Laboratory
Cambridge, CB2 1EW, England

Received May 12, 1971

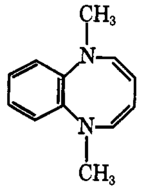
A Synthesis of 1,4-Dithiocins. 1,6-Benzodithiocin[1]

Sir:

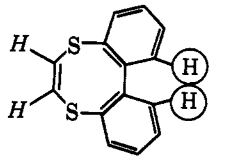
A great deal of effort has been devoted to the synthesis of ten-π-electron systems in recent years.[2] Aromaticity has been demonstrated in certain carbocyclic ring systems but the predictions of the $4n + 2$ rule are not, with one exception,[3] borne out by the ten-π-electron heterocycles synthesized thus far. Following the analogy which furan, pyrrole, and thiophene have with benzene, various heterocyclic analogs of the cyclononatetraenyl anion[4] and the cyclooctatetraene dianion[5] have been prepared and studied. Of the heterocyclic analogs[6] of the former, only 1-H azonine exhibits appreciable aromatic character.[3] Three neutral[7] heterocyclic analogs of the latter have been reported (**1**,[8] **2**,[9] and **3**[10]), none of which exhibits nmr spectral properties consistent with aromaticity in the heterocyclic ring.



1



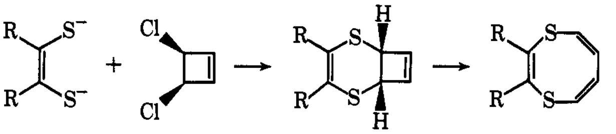
2



3

Despite the nonaromatic character imputed to compound **3** (the italicized protons resonate at 6.26 ppm[10] but steric interactions between the circled protons could destabilize the planar form), there are two good reasons for believing that eight-membered rings with two sulfur atoms may be the best candidates for ten-π-electron aromatic heterocycles. The aromaticity of the cyclooctatetraene dianion demonstrates that 135° bond angles can be accommodated and a sulfur atom is more nearly equivalent to a carbon–carbon double bond than other heteroatoms.[11]

With this incentive we have undertaken a study of 1,4-dithiocins based on the following synthetic scheme and report in preliminary form our results which, contrary to our original expectations, mitigate against the existence of aromatic character in this system.



Salts of the appropriate *cis*-1,2-dimercaptoethenes[12] were found to condense smoothly with *cis*-3,4-dichlorocyclobutene[13] to give 1,4-dithiocin precursors **4** [50%; mp 178–179°; nmr (CDCl$_3$) δ 4.84 and 6.09 ppm (2 H, m, $W_{1/2} \simeq 2$ Hz); and mass spectrum m/e 116, 165, and 192 (M$^+$)], **5** [61%; mp 102–103°; nmr

---

[1] This research was supported by the National Science Foundation (GP-10950) and the Cities Service Oil Co. Presented at the 23rd IUPAC Congress, Boston, Mass., July 1971.

[2] T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784, 3785 (1960); M. Avram, G. Mateescu, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636**, 174 (1960); M. Avram, C. D. Nenitzescu, and E. E. Marica, *Chem. Ber.*, **90**, 1857 (1957); R. C. Cookson, J. Hudec, and J. Marsden, *Chem. Ind.* (*London*), 21 (1961); E. Vogel, W. Meckel, and W. Grimme, *Angew. Chem., Int. Ed. Engl.*, **3**, 643 (1964); E. E. van Tamelen and B. Pappas, *J. Amer. Chem. Soc.*, **85**, 3296 (1963); E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967); S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4804 (1967); G. Schroeder and T. Martini, *Angew. Chem., Int. Ed. Engl.*, **6**, 806 (1967); K. Grohmann and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7119 (1967); R. H. Mitchell and F. Sondheimer, *ibid.*, **90**, 530 (1968); A. P. Bindra, J. A. Elix, and M. V. Sargent, *Tetrahedron Lett.*, 4335 (1968); P. J. Mulligan and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7118 (1967); C. S. Baxter, P. J. Garratt, and K. P. C. Vollhardt, *ibid.*, **91**, 7783 (1969); P. Radlick and G. Alford, *ibid.*, **91**, 6529 (1969); J. Fabian and H. Hartmann, *Tetrahedron Lett.*, 239 (1969); P. J. Garratt and K. A. Knapp, *Chem. Commun.*, 1215 (1970).

[3] A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 825 (1970).

[4] T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964); E. A. La Lancette and R. E. Benson, *ibid.*, **87**, 1941 (1965); G. Boche, D. Martens, and W. Danzer, *Angew. Chem., Int. Ed. Engl.*, **8**, 984 (1969).

[5] C. A. Coulson, *Tetrahedron*, **12**, 193 (1961).

[6] J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. van Auken, *J. Amer. Chem. Soc.*, **90**, 5041 (1968); A. P. Bindra, J. A. Elix, P. J. Garratt, and R. H. Mitchell, *ibid.*, **90**, 7372 (1968); A. G. Anastassiou and J. H. Gebrian, *ibid.*, **91**, 4011 (1969); S. Masamune, S. Takada, and R. T. Seidner, *ibid.*, **91**, 7769 (1969); A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 903, 1521 (1969); S. Masamune, K. Hojo, and S. Takada, *ibid.*, 1204 (1969); A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 5239 (1969).

[7] Azocinyl dianions appear to be also aromatic: L. A. Paquette, T. Kakihana, and J. F. Hansen, *ibid.*, 529 (1970).

[8] W. Schroth and B. Werner, *Angew. Chem., Int. Ed. Engl.*, **6**, 697 (1967).

[9] H-J. Shue and F. W. Fowler, *Tetrahedron Lett.*, 2437 (1971).

[10] W. Schroth, F. Billig, and A. Zschunke, *Z. Chem.*, **9**, 184 (1969).

[11] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, p 28. This is perhaps best illustrated by the close resemblance which thiophene bears to benzene. The rationalization of this resemblance in terms of d orbital contributions to the π-bonding *via* pd^2 hybrids would be applicable to the 1,4-dithiocins. However, this question of d orbital involvement is a highly contentious one. For recent reviews see W. G. Salmond, *Quart. Rev., Chem. Soc.*, **22**, 253 (1968), and D. T. Clark in "Organic Compounds of Sulphur, Selenium, and Tellurium," Vol. 1, The Chemical Society, London, 1970, p 9.

[12] G. Bähr and G. Schleitzer, *Chem. Ber.*, **90**, 438 (1957); W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964); S. Hünig and E. Fleckenstein, *Justus Liebigs Ann. Chem.*, **738**, 192 (1970).

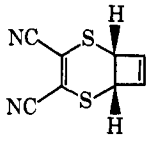
[13] M. Avram, I. Dinulescu, M. Elian, M. Farasiu, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

Table I. Reaction Conditions, Products, and Yields

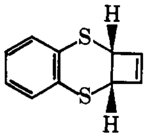
Precursor	200°[a]	400°[b]	$h\nu$[c]
4	Tar	Phthalonitrile (61%) and sulfur (trace)	Phthalonitrile (30%) and sulfur 15%)
5	**7** (11%) and starting material (59%)	Naphthalene (30%), thiophene (5%), sulfur (3%), and four unidentified products	**8** (5%), starting material (50%), and one unidentified product
6	Benzene (50%) and starting material (50%)[d]	Benzene (27%), thiophene (trace), sulfur (13%), and phenyl disulfide (2%)	e

[a] In glass tubes sealed under vacuum. [b] In quartz tube packed with quartz wool at 0.05 mm pressure. [c] Dioxane solutions irradiated for 24 hr with a GE Sunlamp at 50°. [d] After 1 hr, nmr analysis. [e] Irradiation for 5 hr produced a mixture of polymer and unreacted **6**.

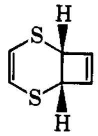
(CCl$_4$) δ 4.50 and 5.78 (2 H, m, $W_{1/2} \simeq 2$ Hz) and 7.21 ppm (AA′BB′ m); and mass spectrum m/e 147 and 192 (M$^+$)], and **6** [32%; mp 49–52°; nmr (CCl$_4$) δ 4.42, 5.86, and 6.70 ppm (2 H, m, $W_{1/2} \simeq 2$ Hz); and mass spectrum m/e 97 and 142 (M$^+$)].



4



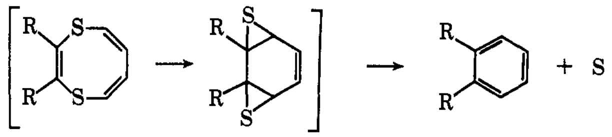
5



6

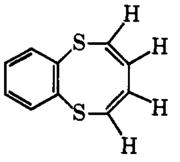
The production of 1,4-dithiocins from **4**, **5**, and **6** requires disrotation if the ring openings are to be synchronous processes. Stepwise processes are highly tenable, however, in view of the stabilizing influences available to radical intermediates. Accordingly, both the photolytic and thermal behavior of these substances were examined. The results are presented in Table I.

The most prominent chemical feature of compounds **4**, **5**, and **6** is their propensity to lose sulfur giving benzenoid aromatics. This reaction pathway is formulated as follows

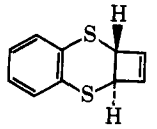


Ring opening to the 1,4-dithiocin is followed by spontaneous valence isomerization (an internal Diels–Alder reaction) leading to bisepisulfides. These can lose sulfur either thermally[14] or photochemically.[15]

Facile desulfurization leading to benzenoid aromatics is a salient feature in the chemistry of thiepines[16] and has been formulated in terms of an episulfide intermediate for that system also.[17] Thiepines neither show nor are expected[18] to show aromatic character. The formation of phthalonitrile, naphthalene, and benzene from compounds **4**, **5**, and **6**, respectively, therefore suggests that there is no significant aromatic stabilization of the corresponding 1,4-dithiocins.



7



8

Under the milder of the two pyrolysis conditions examined (lower temperatures effected no change), compound **5** is partially converted to 1,6-benzodithiocin (**7**). This product was isolated as a yellow oil by preparative tlc and further purified by vacuum distillation (oven temperature 130° (0.05 mm)). Its nmr spectrum consists of two AA′BB′ multiplets of equal areas centered at 6.23 and 7.25 ppm. The signal at 6.23 ppm precludes the presence of a diamagnetic ring current in the heterocyclic ring. Other spectral properties of this compound include: ir (film) bands at 1565, 1600, 2850, 2920, 2950, 2990, 3010, and 3025 cm^{-1}; uv max (cyclohexane) 235 (10,500), 252 (10,800), 278 (3480), and 355 (825); and mass spectrum m/e 147 (100%) and 192 (37%, M$^+$).

Irradiation of compound **7** (sunlamp, cyclohexane, 2 hr) effects quantitative conversion back to compound **5**. Vacuum pyrolysis (quartz tube at 400°) produces naphthalene as expected.

Photolysis of compound **5** produced in low yield a crystalline substance (mp 84–87°) with nmr and mass spectra quite similar to those of **5** itself. This material is accordingly formulated as the trans isomer **8**. The nmr spectrum shows, in addition to the AA′BB′ multiplet centered at 6.96 ppm, two 2 H quartets at 4.28 and 6.48 ppm (J = 1.2 Hz) indicating that the vicinal and allylic coupling constants must be nearly equal in this isomer.

* Address correspondence to Chemical Research Department, Hoffmann-LaRoche Inc., Nutley, N. J. 07110.

D. L. Coffen,* Y. C. Poon, M. L. Lee
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

Received June 28, 1971

---

[14] B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, New York, N. Y., 1957, p 93.

[15] Several examples are listed by E. Block, *Quart. Rep. Sulfur Chem.*, 4, 237 (1969).

[16] G. P. Scott, *J. Amer. Chem. Soc.*, **75**, 6332 (1953); K. Dimroth and G. Lenke, *Chem. Ber.*, **89**, 2608 (1956); J. D. Loudon and A. D. B. Sloan, *J. Chem. Soc.*, 3262 (1962); V. J. Traynelis and J. R. Livingston, *J. Org. Chem.*, **29**, 1092 (1964); W. E. Parham and D. G. Weetman, *ibid.*, 34, 56 (1969); H. Hofmann, H. Westernacher, and H. Haberstroh, *Chem. Ber.*, **102**, 2595 (1969).

[17] R. Grigg, R. Hayes, and J. L. Jackson, *Chem. Commun.*, 1167 (1969).

[18] M. J. S. Dewar and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

Crystal Structure and Spectroscopic Properties of the 1-Azabicyclo[3.3.3]undecane System

Sir:

Bicyclo[3.3.3]undecane (**1**)[1,2] and 1-azabicyclo[3.3.3]-undecane (**2**),[2] prototypes containing three eight-

---

[1] M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrahedron Lett.*, 3619 (1970).

[2] N. J. Leonard and J. C. Coll, *J. Amer. Chem. Soc.*, **92**, 6685 (1970); **93**, 287 (1971).