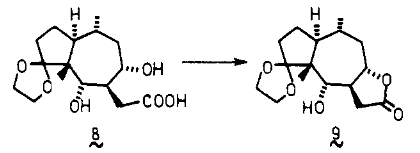
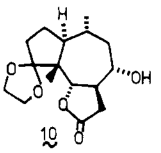
J. Org. Chem. **1981**, *46*, 675–678


8 → 9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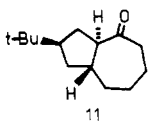
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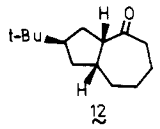
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sional constraints that are imposed upon a cyclic system with the basic ring conformations of the cycle, a primary set of allowed conformations can readily be deduced. The following features have been included in the procedure in order to allow for rapid deduction: torsional constraint evaluation, directly from the α (hashed bond) and β (wedged bond) configurational pattern of the two-dimensional structure; dihedral angle types as a measure for torsion angle magnitudes; linear conformational notations for the unambiguous definition of a conformation in terms of signs and magnitudes of torsion angles at endocyclic bonds. It has been shown that energy and further torsional constraint evaluation reduces effectively the allowable conformations to a small number of preferred ones.

The basic concepts used in the procedure should allow for extension of the present method to other ring systems and for treatment by computer as well.[30] Work on further applications of the present methodology is currently in progress.

Acknowledgment. I thank Professor Hendrickson (Brandeis University) and Dr. Tavernier (this laboratory) for helpful comments about the manuscript. My special gratitude goes to Professor Vandewalle for continuous support of this work. The "Nationaal Fonds voor Wetenschappelijk Onderzoek" and the "Ministerie voor Wetenschapsbeleid" are gratefully acknowledged for financial support to the laboratory.

Registry No. 1, 63568-73-0; 2, 75765-40-1; 3, 73590-08-6; 4, 75765-41-2; 5, 75717-45-2; 8, 75717-46-3; 9, 75766-21-1; 10, 75717-47-4; 11, 70775-29-0; 11 tosylhydrazone, 75765-42-3; 12, 70775-28-9; 12 (*p*-bromophenyl)sulfonylhydrazone, 75765-43-4; cycloheptane, 291-64-5; cycloheptene, 628-92-2.

Supplementary Material Available: A detailed discussion (including Table V) of some observed selectivities in the hydroazulene field: formation of 6 and 7 from 4 and 5, respectively; selective lactonization of 8 to 9; favored formation of 11 in the equilibrium mixture of 11 and 12 (7 pages). Ordering information is given on any current masthead page.

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[30] Upon completion of this work a computer method for the semiquantitative assignment of the conformation of six-membered ring systems has been reported: Corey, E. J.; Feiner, N. F. *J. Org. Chem.* **1980**, *45*, 757, 765.

Phenaleno[1,9-*cd*][1,2,6]thiadiazinium Cation

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Received October 6, 1980

The title ion was prepared in solution in concentrated sulfuric acid by protonation–dehydration of phenaleno[1,9-*cd*][1,2,6]thiadiazine 2-oxide. Its spectral properties (^{1}H NMR, ^{13}C NMR, and UV–visible) have been measured and compared to those for similar ionic systems. The ^{13}C NMR data provided evidence for substantial sulfur d-orbital participation in the overall electronic description of the molecule. The electroreduction of the title species permitted the observation of the phenalenothiadiazinyl radical ESR spectrum. The hyperfine coupling constants provide evidence for spin delocalization into the heteroring portion of the molecule.

Interest in fused ring systems developed in two separate, albeit, closely related directions. In the first, chemists continue their quest for new compounds exhibiting unique physical and chemical properties. In the second emphasis is on the classification of aromaticity based upon molecular conformity with Hückel's rule.[1] Our delvings in this area have emphasized the perturbations caused by insertion of heteroatoms into fused, cyclic conjugated systems. In particular, our attention has centered on the synthesis and examination of tetracyclic peri-bridged napthalenes containing the -NSN-[2] and -NSeN-[3] linkages for the purpose of comparing their properties with those of their known isoelectronic, all-carbon analogues or as predictors of properties of as yet unknown compounds.

Thus, we previously prepared naphthol[1,8-*cd*:4,5-*c′d′*]bis[1,2,6]thiadiazine[2a] (1) and naphtho[1,8-*cd*:4,5-*c′d′*]bis[1,2,6]selenadiazine[3a] (2) as congeners of dipleiadiene (3), a substance which has received theoretical attention[4] but which thus far has defied the preparative chemists.[5]

The molecular and electronic structures of 1 and 2 as deduced spectroscopically[2a,3a] and confirmed by X-ray crystallography[2b,3b] show a strong bond-length alternation, particularly around the periphery of the molecule. This result intuitively leads the chemist to the conclusion that 1 and 2 are antiaromatic 16π systems, one which is at odds

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[1] (a) Hückel, E. *Z. Phys.* **1931**, *70*, 204; (b) *Ibid.* **1931**, *72*, 310. (c) Hückel, E. "Grundzüge der Theorie ungesättiger und Aromatisher Verbindungen"; Verlag Chemie: Berlin, 1938.

[2] (a) Haddon, R. C.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1235. (b) Gieren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *Ibid.* **1979**, *101*, 7277.

[3] (a) Kaplan, M. L.; Haddon, R. C.; Schilling, F. C.; Marshall, J. H.; Bramwell, F. B. *J. Am. Chem. Soc.* **1979**, *101*, 3306. (b) Gieren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *Ibid.* **1980**, *102*, 5070.

[4] (a) Zahradnik, R.; Michl, J.; Pancier, J. *Tetrahedron* **1966**, *22*, 1355. (b) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592.

[5] For one synthetic approach, see: Laycock, D. E.; Wain, R. J.; Wightman, R. H. *Can. J. Chem.* **1977**, *55*, 21.

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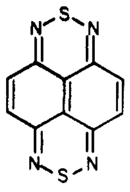
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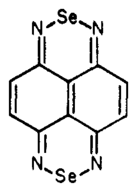
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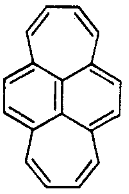
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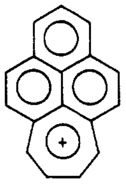
with the extraordinary stabilities observed for these molecules.[2a,3a]

We then undertook to answer the question of what properties could be expected from a similar 14π periphery species containing the N–S–N linkage. Previously, the cyclohepta[*cd*]phenalenium ion (4) had been reported,[6] an example of just such a system. The isoelectronic sulfur-based heteroanalogue (5) has also recently been prepared.[7] Both **4** and **5** are very stable entities, as their tetrafluoborate and hexafluorophosphate salts, respectively, in conformity with expectations for aromatic cations.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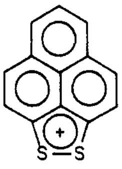
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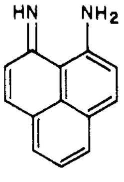
Results and Discussion

The recently published methods for the preparations of 9-amino-1-phenaleneimine (6)[8] suggested that the peripheral 14π-electron cation system containing the N–S–N unit fused to phenalene (7) might be accessible through the application of known experimental procedures. Therefore, when **6** was warmed with *N*-thionylaniline in benzene, phenaleno[1,9-*cd*][1,2,6]thiadiazine 2-oxide (8) was obtained. These conditions approximated those used in the preparation of 1*H*,3*H*-naphtho[1,8-*cd*][1,2,6]thiadiazine 2-oxide[9] (9). Although the dehydration of **9** to naphtho[1,8-*cd*][1,2,6]thiadiazine (10) was effected easily,[9] conversions of **8** to **7** presented some experimental difficulties. Initially the approach used required the treatment of the sulfinimide (8) with strong, anhydrous acid so that protonation followed by spontaneous dehydration would be favored. However, HBF_4 in acetic anhydride,[10] HBF_4 in acetonitrile, HBr in benzene or acetic anhydride and trifluoroacetic anhydride by themselves gave no isolable products except for the salts of the protonated imino amine (6). The salt (11) was independently prepared and characterized as the bromide.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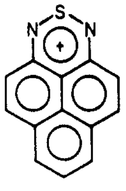
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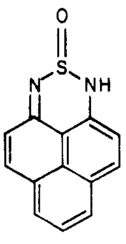
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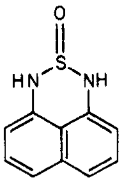
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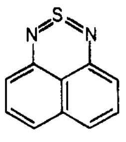
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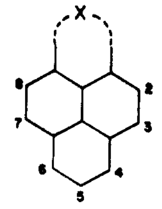
Table I. Electronic Spectra[a] of Several Bridged 14π Phenalenylium Compounds

compd	solvent	λ_{max}, nm	log ε
7[b]	D_2SO_4	202	4.57
		247	4.18
		326	4.65
		402	3.72
		470	3.37
4[c]	CH_3CN	224	4.40
		257	3.99
		291	4.37
		316	4.40
		475	4.49
5[d]	CH_3CN	213	4.53
		226	4.50
		281	3.97
		343	3.75
		439	4.49

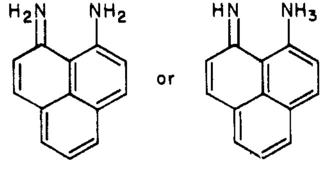
[a] Shoulders have not been included. [b] This work. [c] Reference 6. [d] Reference 7.

Table II. ¹H NMR Chemical Shifts of Phenalenylium Ring Protons



compd	x	H-2,8	H-3,7	H-4,6	H-5
4[a]	$(CH)_4$	9.16	9.50	9.40	9.00
5[b]	S_2	8.44	8.71	8.74	8.23
7[c]	NSN	8.41	9.08	8.95	8.60
12[d]	H, H	8.48	9.30	9.30	8.48
11[e]	NH_2^+, NH_2	7.32	8.20	8.07	7.58

[a] (CD_3CN), ref 6, $J_{2,3} = J_{7,8} = 8.9$ Hz; $J_{4,5} = J_{5,6} = 7.7$ Hz. [b] (CD_3CN), ref 7, $J_{2,3} = J_{7,8} = 9$ Hz; $J_{4,5} = J_{5,6} = 8$ Hz. [c] (D_2SO_4), this work, $J_{2,3} = J_{7,8} = 9$ Hz; $J_{4,5} = J_{5,6} = 7$ Hz. [d] ($AsCl_3$) ref 11, $J = 7.2$ Hz. [e] (D_2SO_4), this work, $J_{2,3} = J_{7,8} = 9.5$ Hz; $J_{4,5} = J_{5,6} = 6$ Hz.


11

Rather than pursue **7** as a stable solid, the problems encountered thus far persuaded us to attempt to form and study the desired-cation in solution. When sulfinimide **8**

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(6) (a) Murata, I.; Yamamoto, K.; Kayane, Y.; *Angew. Chem., In. Ed. Engl.* **1974**, *13*, 808. (b) Yamamoto, K.; Kayane, Y.; Murata, I. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1964.

(7) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629.

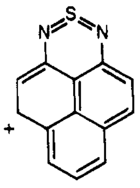
(8) (a) Neidlein, R.; Behzadi, Z. *Chem.-Ztg.* **1978**, *102*, 150. (b) Franz, K. D.; Martin, R. L. *Tetrahedron* **1978**, *34*, 2147. (The reported melting point in this reference is incorrect; the corrected melting point is 186–187 °C.)

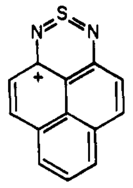
(9) Behringer, H.; Leiritz, K. *Chem. Ber.* **1965**, *98*, 3196.

(10) For the preparation of this reagent see: Wudl, F.; Kaplan, M. L. *Inorg. Synth.* **1979**, *19*, 27.

was dissolved in concentrated D_2SO_4 an orange solution resulted on which spectroscopic determinations were performed. In Table I are found the UV-visible spectra of the 14π cation systems **4**, **5**, and **7**. In Table II are found the chemical shifts and coupling constants derived from the ^1H NMR spectra of **4**, **5**, **7**, **11**, and the phenalenylium cation (**12**).[11] Except for **12**, which is symmetrical, the other substances show typical AB patterns for H-2, H-8, H-3, and H-7 and AB_2 patterns for H-5, H-4, and H-6. The chemical shifts for **7**, between δ 8.41–9.08, exhibit proton deshieldings comparable to what is found for **4**, **5**, and **12** and much greater than that for **11** where the positive charge resides, in large measure, on the nitrogens. This implies that the positive charge for **7** is delocalized over the molecular periphery, consistent with expectations for a 14π aromatic cation.

The ^{13}C spectra are particularly instructive in that they provide some insight into the electronic structure of the various phenalenylium cations. Table III contains a listing of ^{13}C chemical shifts for the eight different types of carbons in molecules **5**, **7**, and **11**. Of these carbons only C-1, C-4, and C-6 could be assigned unambiguously on the basis of examination of line-intensity changes in spectra taken with fast and slow pulse repetition rates. Also in the table are values of charge densities at the various carbons as calculated by standard HMO methods. With reference to carbon number 1 it can be seen that for **7** the chemical shift (δ 154.60) lies between that found for **5** (δ 166.13) and **11** (δ 148.99) but much closer to that for **11**. In **1**, a neutral substance known to exist largely as the quinone imine,[2] the ^{13}C chemical shift of C-1 is δ 161.23.[12] In **10**, also neutral, the sulfur must have a high degree of tetravalency and there the chemical shift of C-1 is δ 143.14.[12] From this we infer that in **7** significant contributions to the overall electronic description come from those structures incorporating tetravalent sulfur, as in **13a–d**. In addition to those canonical forms where d-orbital participation is important, structures such as **13e–h** also augment the full charge delocalization picture.


13a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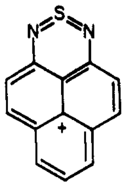
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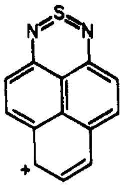
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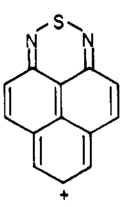
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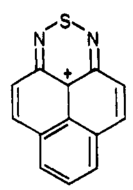
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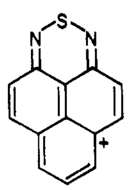
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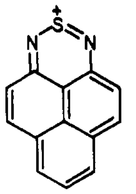
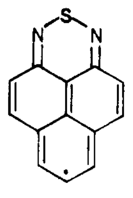
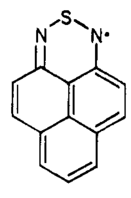
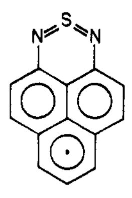

13h

The assignments of ^{13}C chemical shifts of the protonated carbons C-2, C-3, and C-5, and of the quaternary carbons C-7 and C-8 were made solely on the basis of the HMO charge density calculations and are not unambiguous.

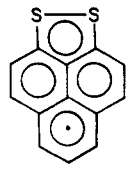
One goal of these investigations was to subject **7** to reduction, thereby providing access to the stable neutral radical **14**. This approach worked well in the case of the isolable **5**, affording the stable 1,9-dithiophenalenyl radical **15**.[7]


14a, etc.


14b, etc.


14c, etc.

In one of the early attempts to dehydrate **8** with fluoboric acid we were able to isolate a BF_4^- salt, containing sulfur, but which was never analytically pure. Nevertheless, it was felt that electroreduction of the impure product in an ESR cavity would allow the observation of the spectrum of **14**. When the radical was generated by reduction in acetonitrile at room temperature, the spectrum obtained was analyzed. The results are presented in Table IV and compared to the parent phenalenyl radical and related substances. The data for **14** are quite similar to the values for **15** and **16** which also appear in Table IV. The HMO–McLachlan calculation of the spin densities in **14** provides a completely different picture with most of the spin erroneously concentrated in the NSN ring rather than phenalenyl unit. This deficiency in the calculations apparently arises from the omission of d orbitals which are of some importance in this system. The ESR coupling constants indicate that **14** is primarily described by structure of the form **14c** and is a perturbed phenalenyl radical analogous to **15** and **16**.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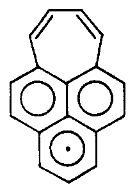
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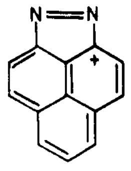
17

While we are convinced that the species formed when thiadiazine oxide **8** is dissolved in concentrated sulfuric acid is the cation **7** we cannot rigorously exclude the azo compound **17** as being responsible for our spectroscopic findings. Such a structure probably would not have the stability that we observe; e.g., sulfuric acid solutions remain unchanged after at least several days at room temperature. In addition, no reasonable structures can be drawn where the positive charge resides on nitrogen. The NMR and ESR spectra of **5** and **7** and **14** and **15** respectively, are too similar to permit consideration of molecules where positive charge is not delocalized into the heteroring. Finally, the mass spectrum of sulfinimide **8** provides evidence for the cation **7** at m/e 223, while not showing any peaks for masses in accord with **17**.

Experimental and Calculational Section

HMO wave functions were obtained with the parametrizations $\alpha_N = \alpha + 0.7\beta$, $\alpha_s = \alpha + 1.1\beta$, $\beta_{C-N} = 1.05\beta$, $\beta_{N-S} = 0.7\beta$, $\beta_{C-S} = 0.65\beta$, and $\beta_{S-S} = 0.7\beta$.[2,15,16]

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[11] Prinzbach, H.; Freudenberger, V.; Scheidegger, V. *Helv. Chim. Acta* **1967**, *50*, 1087.

[12] Unpublished observations of F. C. Schilling, R. C. Haddon, and M. L. Kaplan.

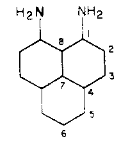
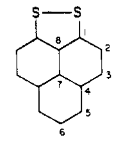
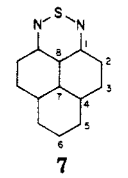
[13] (a) Gerson, F. *Helv. Chim. Acta* **1966**, *49*, 1463. (b) Gerson, F.; Heilbronner, E.; Reddock, H. A.; Paskovich, D. H.; Das, N. C. *Ibid.* **1967**, *50*, 813.

[14] Gerson, F.; Jachimowicz, J.; Murata, I.; Nakasuji, K.; Yamamoto, K. *Helv. Chim. Acta* **1975**, *58*, 2473.

[15] Atherton, N. M.; Ockwell, J. N.; Deitz, R. *J. Chem. Soc. A* **1967**, 771.

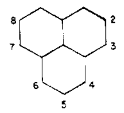
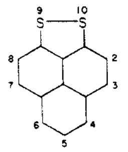
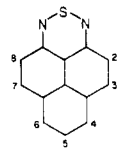
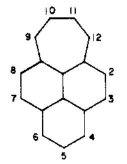
[16] (a) Bechgaard, K.; Parker, V. D.; Pedersen, C. Th. *J. Am. Chem. Soc.* **1973**, *95*, 4273. (b) Bramwell, F. B.; Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H. *Ibid.* **1978**, *100*, 4612.

Table III. ^{13}C NMR Chemical Shifts (δ) of Phenalenylium Compounds and Calculated Charge Densities (HMO-q)

	 11		 5		 7	
position	δ obsd[a]	calcd q	δ obsd[a]	calcd q	δ obsd[a]	calcd q
1	148.99	0.157	166.13	0.121	154.60	0.125
2[b]	123.52	-0.028	122.35	-0.025	125.55	-0.005
3[b]	146.79	0.133	141.08	0.083	145.28	0.069
4	129.64	-0.009	128.65	-0.008	133.32	0.017
5[b]	141.22	0.102	136.04	0.075	137.37	0.059
6	130.38	0.004	130.68	0.004	135.09	0.022
7[c]	123.52	0.001	133.14	0.001	112.12	0.000
8[c]	115.75	-0.027	121.92	-0.030	119.03	0.081

[a] Concentrated D_2SO_4-CH_3SO_3H as secondary standard. [b] Assigned on basis of calculations. [c] Assigned on basis of calculations.

Table IV. Hyperfine Proton Coupling Constants (a_H) of Phenalenyl Radicals

			 15		 14		 16	
positions	obsd[a]	calcd	obsd[b]	calcd	obsd[c]	calcd[e]	obsd[d]	calcd[e]
2, 8	1.820	1.794	1.49	0.71	1.49	1.00	1.55	0.47
3, 7	6.304	6.044	5.06	4.83	5.45	0.82	4.80	4.48
4, 6	6.304	6.044	5.45	5.50	7.14	0.72	5.01	5.17
5	1.820	1.794	1.49	1.471	1.49	0.77	1.36	1.27

[a] CCl_4, ref 13. [b] CH_2Cl_2, ref 7. [c] CH_3CN, this work, $a_N = 1.49$ G. [d] DMF, ref 14, $a_{H_{9,12}} = 0.28$ G (calcd 0.70 G), $a_{H_{10,11}} = 2.95$ G (calcd 2.08 G). [e] Our calculations.

Solution ESR (Varian x-band spectrometer) spectroscopy was performed on the radical 14 prepared by electroreduction of cation 7 at -1.30 V (vs. SCE) in acetonitrile with n-Bu_4NBF_4 as supporting electrolyte.

^{13}C NMR spectra were measured on a Bruker WH-90 spectrometer (22.62 MHz) in concentrated D_2SO_4 at ambient temperature. Concentrations of samples were 100 mg/mL for molecules 7 and 11 and 200 mg/mL for molecule 5. Approximately 1000 scans were accumulated on each sample at pulse repetition times varying from 4.0 to 60.0 s. The secondary chemical shift standard was CH_3SO_3H. Proton spectra were obtained with a Bruker WH-90 or Varian T-60A spectrometer. Electronic spectra were taken with a Perkin-Elmer 330 spectrometer and IR spectra with Perkin-Elmer 597 spectrometer. C, H, N analyses were performed on a Perkin-Elmer 240 elemental analyzer.

Mass spectra were determined by Gollob Analytical Service, Berkley Heights, NJ.

Phenaleno[1,9-*cd*][1,2,6]thiadiazine 2-Oxide (8). To a solution of 9-amino-1-phenalenimine (0.58 g, 3 mmol) in 15 mL of benzene was added N-thionylaniline (0.42 g, 3 mmol). After being stirred under N_2 at ~50 °C the initially homogeneous solution deposited an orange-brown solid. After 2 h the precipitate was collected, washed with benzene, and dried under a N_2 stream to give 0.24 g of solid. The filtrate was stirred under N_2 at ~50 °C for 16 h with additional 3 mmol of N-thionylaniline. The precipitate which formed was again collected, washed with benzene, and dried under N_2 to give a further 0.28 g of solid. The total yield was 0.52 g, corresponding to 72%: mp, 154.5–155 °C; IR (CsI) 3060 (s, br), 1640 (s), 1570 (s), 1500 (s), 1400 (m), 1348 (s), 1290 (w), 1238 (m), 1180 (m), 1147 (m), 1133 (m), 1073 (vs), 1000 (m), 970 (w), 838 (s), 813 (s), 740 (w), 695 (m), 612 (w), 565 (w), 520 (w), 435 (w), 345 (w) cm^{-1}; UV (EtOH) λ_{max} nm 243 (ϵ 30900), 272 (sh, 9710), 280 (sh, 7060), 297 (sh, 2650), 351 (12500), 364 (15800), 437 (5540); ^1H NMR (Me_2SO-d_6, Me_4Si) AB pattern, δ_A 7.47, δ_B 8.32 (J_{AB} = 9.5 Hz), AB_2 pattern, δ_A 7.71, δ_B 8.14 (J_{AB} = 5.2 Hz); mass spectrum showed no molecular ion at m/e 240 but showed a strong peak at m/e 223 corresponding to $C_{13}H_7N_2S^+$. Anal. Calcd for $C_{13}H_8N_2OS$: C, 64.99; H, 3.35; N, 11.66. Found: C, 65.11; H, 3.38; N, 11.48.

1-Phenaleneimine-9-aminium Bromide (11). Through a slurry of sulfinimide (8) in dry benzene was bubbled anhydrous HBr. The solid which resulted was recrystallized from 1,2-dichloroethane to give red needles: IR (CsI) 3390 (s), 3330 (s), 3280 (s), 3150 (vs, br), 1680 (s), 1640 (s), 1592 (m), 1565 (s), 1510 (m), 1493 (w), 1464 (m), 1355 (m), 1335 (s), 1244 (s), 1188 (s), 1168 (s), 1050 (m), 955 (w), 932 (w), 843 (s), 819 (m), 713 (m), 705 (m), 671 (w), 540 (m), 460 (m) cm^{-1}; UV (EtOH) λ_{max} nm 247 (ϵ 28900), 270 (sh, 10800), 297 (sh, 3930), 310 (3640), 320 (3610), 335 (5590), 351 (11700), 371 (17300), 410 (sh, 3720), 435 (7340), 459 (9430). Anal. Calcd for $C_{13}H_{11}N_2Br$: C, 56.75; H, 4.03; N, 10.18. Found: C, 56.79; H, 4.18; N, 10.16.

Registry No. 5, 68377-40-2; 7, 75961-51-2; 8, 75949-37-0; 11, 75949-38-1; 14, 76010-10-1; 16, 76010-11-2; 9-amino-1-phenalenimine, 67618-27-3; N-thionylaniline, 1122-83-4.