$$RO-\underset{|}{\overset{|}{C}}-SO_3^- \cdot HA \rightleftharpoons \left[RO \overset{+}{-} C \overset{}{\underset{}{\diagdown}} SO_3^- \cdots H \cdots \overset{-}{A} \right]^{\ddagger}$$

$$\rightleftharpoons R\overset{+}{O}=C \overset{}{\underset{}{\diagdown}} \cdot SO_3H^- \cdot A^- \quad (12)$$

hydrogen-bonded complex, $SO_3^{2-} \cdot HA$, to the oxocarbonium ion. The fact that the values of α and ρ for the rate constants are approximately half of those for the equilibrium constants for complete proton transfer and C–S cleavage, respectively, support a central transition state as shown in Figure 7.[23]

The principal driving force for catalysis of this reaction by the mechanism of eq 8 arises from the instability of the sulfonic acid intermediate in the upper left corner of the diagram of Figure 7. The reaction mechanism avoids this intermediate by following a path near the center of the diagram. The pK_a of the free sulfonic acid has been estimated to be approximately $-8^{2,24}$ and there is, therefore, a strong driving force for avoiding its formation by hydrogen bonding to a buffer base. General acid catalysis of most carbonyl addition reactions involves proton donation to the carbonyl oxygen atom through a class e mechanism (e.g., eq 9) and we are not aware of a well-established precedent for the specific acid–general base catalysis addition mechanism of eq 8 in which the carbonyl group is protonated in an initial fast step, followed by general base catalysis of nucleophile attack. There is no evidence for bifunctional acid–base catalysis involving both the carbonyl and sulfite groups because the rate constants for catalysis by bifunctional acids do not fall above the Brønsted line that passes through the catalytic constant for the proton, which is not capable of bifunctional catalysis, and because there is no large increase in rate relative to the α-methoxysulfonic acid, which is not subject to bifunctional catalysis. The class n mechanism is presumably observed in this reaction because of the very low nucleophilicity of HSO_3^-, the instability of the product formed from the addition of HSO_3^-, and the fact that catalysis of this kind is enforced by the diffusion-controlled reaction of SO_3^{2-} with the oxocarbonium ion. The fact that the observed catalysis is somewhat less than that estimated from the Hine equation[10] suggests that the value of $\tau = 0.024$ used to estimate K_{AB} from this equation may be too large.

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Naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine.
A Compound of Ambiguous Aromatic Character

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Abstract: The synthesis and chemical and physical properties of the title compound are reported. Naphtho[1,8-*cd*:4,5-*c'd'*]-bis[1,2,6]thiadiazine (5) is found to possess the chemical stability normally associated with an aromatic compound but its electrochemistry, electronic spectrum, and ^{1}H NMR chemical shift suggest that the compound is antiaromatic. On this basis it is concluded that 5 is a compound of ambiguous aromatic character. It is pointed out that many of the traditional measures of aromatic character are non-ground-state properties when applied to certain classes of compounds (including 5). The chemical stability of the molecule is explained on the basis of the chemical inertness of the –NSN– linkage (relative to other structural units).

In attempting to test the generally accepted definitions of aromaticity chemists have synthesized many new compounds with unusual chemical and physical properties.[1] It is generally held that certain of these properties, in conjunction with various structural classifications, may serve as arbiters of the aromatic character of any new material. Among these tests for aromatic character, the foremost seem to be the resonance energy and ring current criteria, although other evi-
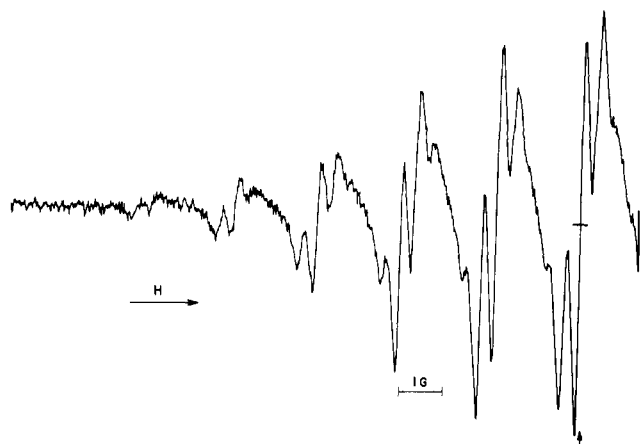
Figure 1. Low-field portion of the ESR spectrum of the radical anion of **5** in acetonitrile.

dence is often cited (chemical reactivity/stability, ease of formation. electronic spectrum, electrochemical behavior, ionization potential/electron affinity).[1,2] The presumption in such an analysis is that the classification of the aromatic character of a compound by any one criterion necessarily reflects on the other properties which are traditionally associated with this class of compounds. There is an increasing body of evidence which suggests that parallels of this type only occur under rather restrictive conditions[3-5] and we have recently proposed that alternant hydrocarbons are the only group of compounds which can hope to fulfill this generalization [as nonalternants lose the vital symmetry between the ground and excited state manifolds (see later)].[5]

A typical example of the confusion caused by unwarranted extrapolation of chemical and physical properties relating to aromatic character is provided by pyracylene (**1**).[6-14] The compound was first synthesized by Trost and co-workers,[7] who labeled **1** a perturbed [12]annulene on the basis of its NMR chemical shifts, electronic spectrum, and electrochemical behavior. We take this classification to mean that the configurations **1b** and **1c** contribute equally to the electronic ground state of **1**.

1a   **1b**   **1c**
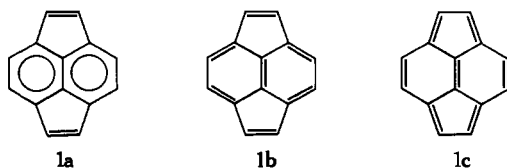
Other workers have concluded, by theoretical analysis or reinterpretation of the data, that **1** is unstable[8] (antiaromatic), pentalenoid,[6-9] nonazulenoid,[10] aromatic,[11] or better represented by **1a**,[12,13] or adopted some middle ground.[14] Current interest has now turned to dipleiadiene (**2**), which together with acepleiadylene (**3**)[15] will presumably complete the trio of nonalternant tetracyclic peri-bridged naphthalenes (**1-3**).


2   **3**   **4**
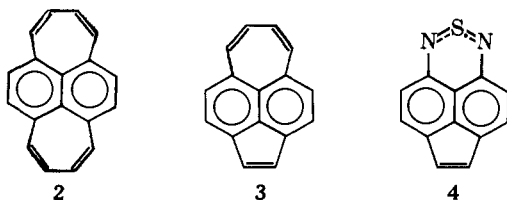
In a similar connection (see below), we also note the revival of interest in the sulfur–nitrogen bond as a result of the singular behavior of $(SN)_x$. which has proved to be not only metallic, but the first polymeric superconductor.[16] In addition a number of heterocycles containing the –NSN– linkage have become

Table I. Electrochemistry

| | Half-wave potentials, V | | | |
Compd	$E_{1/2}^{ox}$ (1)	$E_{1/2}^{red}$ (1)	$E_{1/2}^{red}$ (2)	Ref
1		−1.056	−1.635	7
Naphtho[1,8-*cd*]-[1,2,6]thiadiazine	+1.0	−0.96	−1.8	18e
5	+0.75	−0.77	−1.38	

available for study in recent years.[17,18] In particular, attention has been drawn to the similarities between acenaphtho[5,6-*cd*][1,2,6]thiadiazine (**4**) and **3**, which are isoelectronic,[18f] as the –NSN– unit contains four π electrons. In this paper we report the synthesis and properties of naphtho[1,8-*cd*:4,5-*c'-d'*]bis[1,2,6]thiadiazine (**5**), a molecule isoelectronic with **2**. For reasons discussed more fully below we felt that **5** might

5a   **5b**   **5c**   **5d**
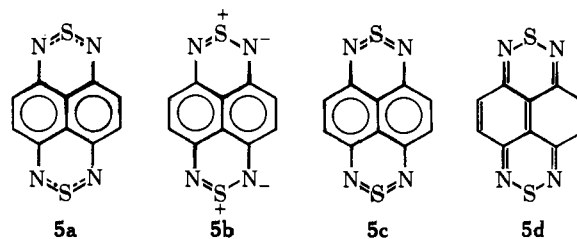
possess some antiaromatic properties (owing to the accessibility of configurations such as **5d**), but also might be stable in the sense of an aromatic compound (as a result of the chemical inertness of the –NSN– linkage). In this way we saw **5** as an ideal test case for the concept of ambiguous aromatic character. As shown below **5** does seem to exhibit chemical and physical properties normally associated with both aromatic and antiaromatic compounds.[1,2]

Results

The title compound was prepared according to reaction 1 in approximately 35% yield (on the assumption that the "tin double salt" of Will[19,20] has the composition shown).

$$SnCl_4 \cdot 2HCl + (C_2H_5)_3N + SO_2 \longrightarrow 5 \quad (1)$$
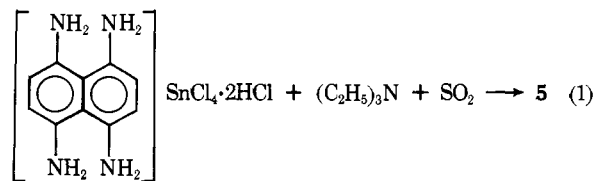
The compound recrystallizes as lustrous, metallic green needles which are indefinitely stable to the atmosphere and melt at ~290 °C. It has poor solubility properties in the usual organic solvents (giving rise to orange solutions).

Our efforts to prepare naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]-selenadiazine were unsuccessful. Attempts to prepare naphtho[1,8-*cd*][1,2,6]selenadiazine via Sachs' procedure[17b] did indeed give rise to a "dicker schwarzer niederschlag", but the material proved to be totally intractable, and the elemental analysis did not correspond to the desired product.

Electrochemistry. The half-wave polarographic potentials for **5** are summarized in Table I, together with data on related molecules.[7,18e] It may be seen that **5** is readily oxidized or reduced in acetonitrile. Although our measurements were hindered by the poor solubility of the compound, all waves appeared to be reversible, with the possible exception of the second reduction. It is interesting to note that the structurally similar tetracyanoquinoquinazalinoquinazoline cannot be oxidized below the dianion.[22]

ESR Spectroscopy. The hyperfine coupling constants derived from the ESR spectra (Figures 1 and 2) of the radical ions of **5** are collected in Table II. They are compared with

Table II. Observed and Calculated Hyperfine Coupling Constants for **5**

| Ion | Atom | Calcd spin spin density (ρ_x) | | Hyperfine coupling constants (a_x, G) | | |
		HMO	McLachlan ($\lambda = 1.0$)	HMO	McLachlan ($\lambda = 1.0$)	Obsd
Anion	H	0.087	0.090	2.53	2.61	2.235
$g = 2.00253$	N	0.097	0.111	2.25	2.59	1.861
	S	0.0	−0.017			
Cation	H	0.012	−0.004	0.35	0.12	0.30
$g = 2.00560$	N	0.104	0.124	2.41	2.89	1.20
	S	0.201	0.235			

Table III. Experimental Naphthalenic Proton Chemical Shifts

Compd	δ (ppm)	Solvent	Ref
5	4.45	CS_2	
1	6.52	CCl_4	7
Naphthalene	7.38	CCl_4	a
Pyrene	8.00	CCl_4	a
3	7.85, 8.23		b
4	8.13, 8.93	$CDCl_3$	18f

a C. W. Haigh and R. B. Mallion, *Mol. Phys.*, **18**, 737 (1970). *b* T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); A. J. Jones, P. D. Gardner, D. M. Grant, and V. Boekelheide, *J. Am. Chem. Soc.*, **92**, 2395 (1970).

values calculated from HMO wave functions (via the McConnell relationship)[23a] and from the McLachlan configuration interaction procedure,[23b] using parameters recommended by previous workers.[18e,i] Such a scheme has not been particularly satisfactory for thiadiazines,[18e] and our own results suggest that the approach is of qualitative significance at best for **5**.

The deviations of the observed *g* values from the free-electron value (2.0023) bear a close relationship to the calculated spin densities at sulfur (the only atom which is sufficiently heavy to give rise to a significant spin–orbit coupling). In fact the molecular orbital which is calculated to contain the unpaired electron in the radical anion of **5** is antisymmetric with respect to a plane containing the long axis of the molecule and perpendicular to the molecular plane (see Discussion). Thus the coefficient of the $2p\pi$ orbital at sulfur is zero by symmetry (in the absence of spin polarization); on the other hand, the 3d orbitals are of the correct symmetry to mix into this orbital. The absence of any large deviations from the free-electron *g* value substantiates earlier suggestions regarding the relatively minor role played by 3d orbitals in influencing the spin densities in such molecules.[18e,i] Thus, the ESR results suggest that structure **5c** may not be a major contributor to the electronic structure of **5**. Analogous conclusions have been reached regarding the electronic structure of **4** (owing to the similarities between **4** and the corresponding triazine).[18f]

NMR Spectroscopy. The proton chemical shift of **5** is compared with the values of some related molecules in Table III. Given the fact that a paramagnetic ring current has been claimed for pyracylene (**1**), on the basis of the ^1H NMR spectrum "which show(s) the protons shifted to exceptionally high fields",[7] it seems safe to assume that the same condition holds true for **5**.[24] Support for this proposition is provided by the ring currents calculated with the McWeeny formulation[25a] of the London theory[25b] and presented in Table IV. Solubility problems have precluded our measurement of the ^{13}C NMR chemical shifts.

Discussion

It is apparent from the previous section that the physical properties of **1**[7] and **5** have many common features. Specifically we note that both compounds exhibit facile reduction, low energy electronic transitions, and evidence for paramagnetic
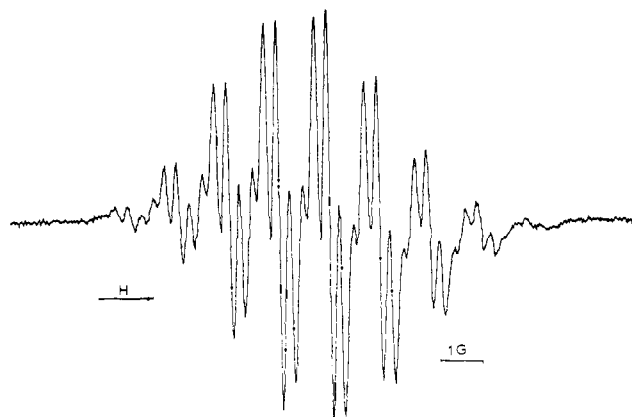
Figure 2. ESR spectrum of the radical cation of **5** in nitrobenzene.

ring currents. *We wish to stress that these results merely indicate the presence of a low-lying manifold of excited states.*[26,27] While this is commonly appreciated in the case of reduction potentials and electronic spectra, it is important to note that this also holds true for ring currents in nonalternant hydrocarbons (and heterocycles).[5] In short, none of these properties *necessarily* makes a definitive statement regarding the ground states of **1** or **5**; in fact (as shown below), in spite of the similarities in their properties, the ground states of **1** and **5** are of entirely different character.

The signs of the coefficients of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of **1** and **5** are shown below (as calculated

1(HOMO)   1(LUMO)   5(HOMO)   5(LUMO)
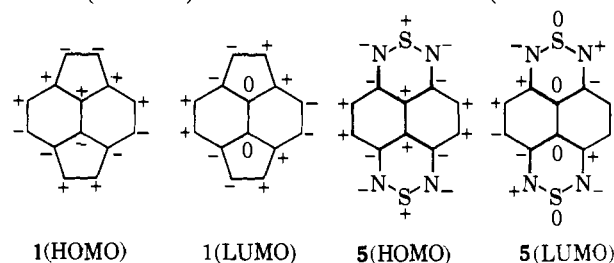
by HMO theory). It is well known that the HOMO is particularly important in determining many molecular ground state properties (particularly bond lengths).[2] On this basis it seems natural to interpret the ground state properties of **1** in terms of configurations such as **1a** and **1b**, whereas the ground state of **5** must be expected to include contributions from configurations such as **5d**. Clearly the LUMO (and first excited state) of **1** would be correlated with configuration **1c**. Molecular structures or resonance energies (if an appropriate reference could be found) would be definitive in this respect. Most calculations[12,13] seem to agree that the ground state electronic structure of **1** is best represented in terms of aromatic and olefinic components (**1a** and **1b**). This seems to afford a reasonable approach to the high reactivity of **1** (another non-ground-state property). We note that antiaromaticity is rarely advanced to account for the high self-reactivity of styrene, and as in the case of **1**, transition state stabilization affords the most

**Table IV.** Calculated Ring Currents (as a Ratio to the Benzene Value)

| Molecule | Naphthalene rings | Peri rings | | | Ref |
		Five-membered	Seven-membered	Six-membered	
1	−0.388	−2.321			a
2	−0.700		−2.861		14
3	1.207	1.115	1.170		14
4	1.115	1.087		1.158	
5	−0.935			−2.056	
Pyrene	0.963			1.327	b
[Pyrene]²⁻	−1.171			−1.452	
Naphtho[1,8-cd][1,2,6]thiadiazine	0.802			−0.152	

a See also ref 14. *b* C. W. Haigh, R. B. Mallion, and E. A. G. Armour, *Mol. Phys.*, **18**, 767 (1970).

logical explanation. It is this consideration which led us to choose **5** as a synthetic target in our hope of finding a molecule of ambiguous aromatic character, that is, the known stability of the -NSN- linkage toward self-reaction. This point is clearly demonstrated by the metallic nature of (SN)$_x$.

Most pseudo-one-dimensional organic materials with a partially filled electronic band structure are unstable toward a Jahn-Teller (or Peierls) distortion.[31] Where there is no suitable distortion coordinate (to introduce a gap in the density of states), the molecules naturally become highly reactive. This results from the pseudo-metalloid character of the material in which state many chemical reaction processes are greatly facilitated. With a work function of 4.81 eV, graphite[32] has a much lower ionization potential and a much higher electron affinity than microscopic organic compounds.

Well-recognized examples of the above behavior are provided by the linear polyenes or annulenes[31,33,34] and the polyacenes.[33,35] The linear polyenes and annulenes (at long chain length) exhibit simple bond-length alternation[31,33,34] as a result of their half-filled band structure and the limiting ionization potential is about 7 eV.[36] On the other hand, the linear polyacenes lack the necessary distortion coordinate to introduce a gap into the density of states,[33,35] and the ionization potentials show a monotonic decrease (benzene, 9.24 eV; naphthalene, 8.15 eV; anthracene, 7.40 eV; tetracene, 7.01 eV; pentacene, 6.64 eV).[37] The larger polyacenes are highly unstable[38] and by analogy with the linear polyenes probably react by conversion of carbon-carbon π bonds to σ bonds, which is thermodynamically favored. It is this factor which probably accounts for the stability of (SN)$_x$ and **5**. (SN)$_x$ is chemically remarkable for two reasons: it does not undergo a distortion, and, in spite of its metallic character, it is chemically stable toward self-reaction. This latter consideration may be ascribed to the weakness of the nitrogen-nitrogen single bond (which is less than half as strong as the carbon-carbon single bond). As a result it seems reasonable to assume that reaction 2 is

(2)
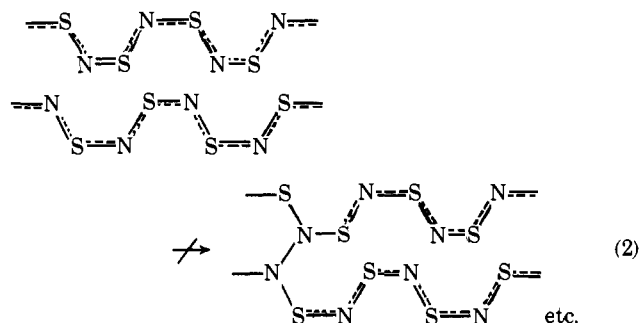
thermodynamically unfavorable. Similar considerations apply to the chemical stability of **5**.

These points would seem to militate against (SCH)$_x$ as a stable metallic polymer, and we note that the -(R)CSC(R)- linkage[39,40] does not enjoy the same high stability of the

thiadiazine unit.[18] It appears that the -(R)CSC(R)- linkage is only stable when R provides conjugative stabilization and/or steric hindrance toward reaction at carbon.[39,40] We believe that these considerations will be important in designing new conducting organic materials,[40] and organic molecules of ambiguous aromatic character.

Conclusions

Naphtho[1,8-cd:4,5-c′d′]bis[1,2,6]thiadiazine (**5**) has the chemical stability normally associated with an aromatic compound, but its electrochemistry, electronic spectrum, and ¹H NMR chemical shift suggest that the compound is antiaromatic. It is concluded that **5** is a compound of ambiguous aromatic character. It is pointed out that many of the traditional measures of aromatic character are non-ground-state properties in certain circumstances as in the case of **5**. The chemical stability of the molecule is explained on the basis of the chemical inertness of the -NSN- linkage (relative to other structural units).

Experimental and Calculational Section

HMO wave functions for use in the calculation of spin densities[23] and ring currents[25] were obtained with the parameterization of Atherton and co-workers:[18e] $\alpha_N = \alpha + 0.7\beta$, $\alpha_S = \alpha + 1.1\beta$, $\beta_{C-N} = 1.05\beta$, and $\beta_{N-S} = 0.7\beta$. Experimental spin densities (ρ_x) were derived from the observed coupling constants (a_x) by use of the relationship[23] $a_x = Q_x\rho_x$, with $Q_H = 29.2$ G, $Q_N = 23.3$ G.[18e]

The cyclic voltammetry on **5** was carried out in acetonitrile with 0.1 M n-Bu₄NBF₄ as supporting electrolyte, with a platinum working electrode and silver/silver chloride reference electrode. The results in Table I are corrected (−0.02 V) to the SCE scale.

The ESR spectra of the radical anion was obtained by electroreduction of **5** at −0.9 V (SCE) in acetonitrile with n-Bu₄NBF₄ as supporting electrolyte. Spectra of the radical cation were obtained by bubbling a small amount of bromine through a solution of **5** in nitrobenzene. The spectra were obtained with an x-band ESR spectrometer utilizing 100-kHz field modulation.

Preparation of Naphtho[1,8-cd:4,5-c′d′]bis[1,2,6]thiadiazine. To a slurry of 1,4,5,8-tetraaminonaphthalene "tin double salt"[19,20] (0.70 g) in ~50 mL of dry methylene chloride was added 6 mL of distilled triethylamine. The mixture was magnetically stirred while anhydrous SO₂ was passed into the flask for 2 h. At the start the reaction was quite exothermic and cooling was effected by placing a water bath around the flask.

The mixture was quenched by adding it to several hundred milliliters of water. A gummy solid formed on the surface and was collected by filtration. The filtrate was extracted with CH₂Cl₂ several times and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated to dryness under reduced pressure. The resulting solid was recrystallized from 1,2-dichloroethane to give metallic green needles (40 mg). The gummy solid collected above was also recrystallized from 1,2-dichloroethane to give metallic green needles (75 mg). The crystals melted at 288–290 °C (uncorrected: sealed tube).

The NMR spectrum in CS₂ (Me₄Si) consisted of a singlet at δ 4.45. The MS showed a molecular ion at m/e 244 together with strong peaks at m/e 216, 172, 122, 120, 70, 69, and 45. The IR spectrum (CsI) gave

rise to lines at 3049 (vw), 1586 (m), 1400 (m), 1351 (m), 1255 (vw), 1131 (s), 1100 (m), 964 (w), 839 (s), 823 (vs), 788 (vs), 752 (vs), 737 (s), 610 (vw), 535 (w), 498 (s), 460 (vs), 335 cm^{-1} (s); there were no detectable absorptions in the N–H or S–H regions of the spectrum. The UV spectrum (CH$_3$CN) exhibited the following: λ_{max} (ϵ) 255 (24 000), 273 (25 500), 335 (sh) (4500), 352 (sh) (4000), 459 (14 000), and 489 nm (19 300). Anal. Calcd for C$_{10}$H$_4$N$_4$S$_2$: C, 49.17; H, 1.65; N, 22.93. Found: C, 49.19; H, 1.91, 1.81, 1.67; N, 23.02.

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