# (Pyridinylmethylidene)dithioles: Synthesis, Structure, and Reactivity

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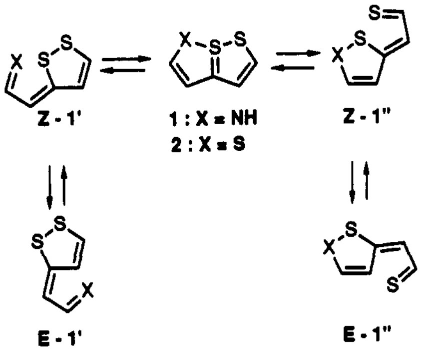
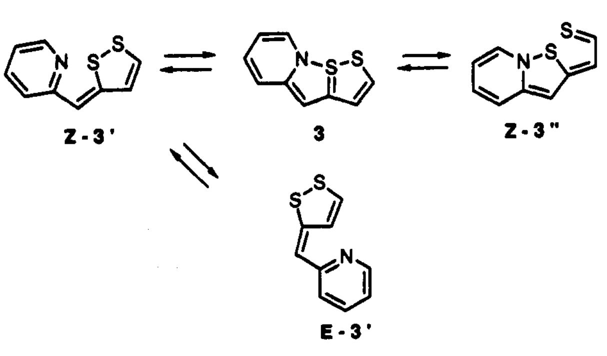
Spectral characteristics, an X-ray crystal structure, and molecular orbital calculations indicate that (pyridinylmethylidene)dithioles **3**, prepared from butadiynyl precursors **4** and hydrogen sulfide in basic methanol, are analogous in their bonding to the parent 1-aza-6,6a$\lambda^4$-dithiapentalenes **1** which, according to ab initio studies at the Hartree–Fock level, is best represented as an (iminomethylidene)dithiole. An interaction between the sulfur and the nitrogen atoms is evident from the significant polarization of the S–S bond in those isomers where the nitrogen is proximal to the dithiole moiety. A comparison of the calculated structures of **1** and **3** with experimental data, as well as preliminary calculations on the related system trithiapentalene **2**, suggest that ab initio methods using a single determinant are inadequate to describe these hypervalent sulfur systems. For example, an asymmetric structure is calculated to be the minimum energy form for **2** in contradiction to experimental results. Electrophilic substitutions, ring rearrangement, and reaction with electron acceptors are described for **3**.

The structure and reactivity of 1-aza-6,6a$\lambda^4$-dithiapentalene **1** and its derivatives have continued to attract interest over a number of years.[1] While these heterocycles and others related to trithiapentalene **2** are often represented as heterocyclic analogues of the aromatic hydrocarbon, pentalene dianion, the precise nature of bonding remains unclear. An early view of the systems included resonance structures lacking a $\sigma$ bond joining the central sulfur atom and one of its neighboring heteroatoms,[1d] the so-called "no bond resonance" form. Compound **1** may be envisioned as an imino dithiole **1′** or as an isothiazolyl thioaldehyde **1″**, or as the fused bicyclic aromatic system **1**. To the extent the bicyclic form is the more correct representation of **1**, annulation of a phenyl ring to the 1,2-side of **1** should provide a significant perturbation as suggested by the resulting structures, (pyridinylmethylidene)dithiole **3′** or benzoisothiazolyl thioaldehyde **3″**. Our interest in systems such as **3** was to investigate their structure and reactivity with reference to **1**, as well as to examine their potential as substrates in charge transfer complexes.

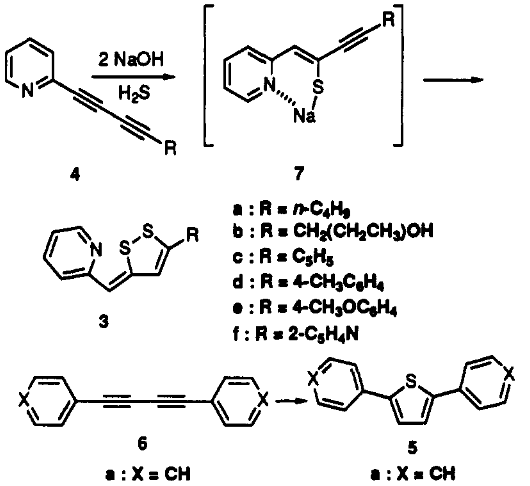




## Synthesis and Structure

Our synthesis of **3** utilized the reaction of hydrogen sulfide with the unsymmetrically substituted butadiynylpyridines.[2] Butadiynes and basic hydrogen sulfide are known[3] to furnish thiophenes in good yield. We have found that an excess of hydrogen sulfide in methanol in the presence of 2 equiv of NaOH (room temperature) reacts with butadiynes **4** to provide the dithiole derivatives **3** as yellow to orange-red products in moderate yields (Table I) as well as varying amounts of the corresponding thiophenes. Using more than 2 equiv of sodium hydroxide did not improve the yield and, in certain cases, provided a product more difficult to purify. The distinctive UV absorption of the thiophenes and the dithioles provided a convenient method for analyzing the reaction mixtures for their respective components.

The 2-pyridinyl substituent apparently facilitates the double addition of hydrogen sulfide via the intermediacy of a complex such as **7**. The involvement of such a complex is substantiated by the conversion of 1,4-diphenylbuta-1,3-diyne (**6a**) under the same reaction conditions exclusively into the thiophene **5a**. Furthermore, the electronically similar compound, 1,4-di(4-pyridinyl)buta-1,3-diyne (**6b**), furnished only thiophene **5b**.



a : R = $n$-$C_4H_9$
b : R = $CH_2(CH_2CH_3)OH$
c : R = $C_6H_5$
d : R = 4-$CH_3C_6H_4$
e : R = 4-$CH_3OC_6H_4$
f : R = 2-$C_5H_4N$

**6**: a : X = CH; b : X = N

**5**: a : X = CH; b : X = N

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† Department of Chemistry.

‡ Corporate Research & Development Center.

[1] (a) Klingsberg, E. *J. Am. Chem. Soc.* **1968**, *33*, 2915. (b) Dingwall, J. G.; Ingram, A. S.; Reid, D. H.; Symon, J. D. *J. Chem. Soc.* **1973**, 2351. (c) Burgot, J.-L.; Vialle, J. *Bull. Soc. Chim. Fr.* **1976**, 1499. (d) Giacometti, G.; Rigatti, G. *J. Chem. Phys.* **1959**, *30*, 1633. (e) Christie, R. M.; Reid, D. H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 848.

[2] Nye, S. A.; Potts, K. T. *Synthesis* **1988**, 375.

[3] Schulte, K. E.; Reisch, J.; Horner, L. *Angew. Chem.* **1960**, *72*, 920.

0022-3263/92/1957-3895$03.00/0

**Table I. (Pyridinylmethylidene)dithioles 3**

| compd no.[a] | R | yield, % | mp, °C | molecular formula | analytical data calcd/found C | H | N | M$^+$ (rel int) [fragment ion] | electronic spectrum $\lambda_{max}$, nm | NMR spectral data $^1$H NMR CDCl$_3$ (ppm) | $^{13}$C NMR CDCl$_3$ (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **3a** | $n$-$C_4H_9$ | 38 | 63–64 | $C_{13}H_5NS_2$ | 62.61<br>62.57 | 6.06<br>6.07 | 5.62<br>5.52 | 249 (100) | 297, 408 | 8.59, 7.56, 7.13, 6.94, 6.74, 6.63, 2.64, 1.65, 1.42, 0.92 | 155.4, 155.1, 154.1, 145.0, 135.5, 123.1, 120.7, 117.5, 110.1, 32.0, 31.9, 22.1, 13.7 |
| **3b** | 1-$OHC_3H_8$ | 24 | 112–114 | $C_{12}H_{13}NOS_2$ | | | | | 290, 409 | 8.69, 7.59, 7.16, 6.97, 6.82, 6.79, 1.63, 1.56 | 163.4, 155.2, 153.9, 144.9, 135.6, 121.2, 120.9, 117.7, 72.9, 31.3 |
| **3c** | $C_6H_5$[b] | 30 | 151.5–153 | $C_{15}H_{11}NS_2$ | 66.88<br>66.96 | 4.12<br>4.18 | 5.20<br>5.16 | 269 (100) | 442 | 8.61, 7.67, 7.27, 7.26, 7.15, 6.98 | 155.1, 153.8, 152.0, 144.7, 135.5, 129.2, 128.6, 126.7, 122.3, 120.9, 117.7, 111.6 |
| **3d** | 4-$CH_3C_6H_4$[c] | 36 | 191–194 | $C_{16}H_{13}NS_2$ | | | | 283 (100) | 444, 427 | 8.59, 7.66, 7.51, 7.21, 7.19, 7.16, 7.01, 6.97, 2.39 | 155.7, 153.4, 152.6, 144.3, 139.7, 136.3, 129.4, 126.6, 122.0, 120.9, 117.8, 111.0, 110.5, 21.2 |
| **3e** | 4-$CH_3OC_6H_4$[d] | 55 | 192.5–193 | $C_{16}H_{13}NOS_2$ | 64.18<br>64.20 | 4.38<br>4.34 | 4.68<br>4.55 | 299 (100) | 442, 426 | 8.61, 7.56, 7.28, 7.18, 7.09, 6.94, 6.92, 6.88, 3.85 | 160.6, 155.5, 154.2, 152.1, 144.9, 135.7, 128.2, 126.8, 121.1, 121.0, 117.7, 114.2, 111.2, 55.4 |
| **3f** | 2-$C_5H_4N$ | 45 | 213.5–214 | $C_{14}H_{10}N_2S_2$ | 62.19<br>62.02 | 3.73<br>3.85 | 10.36<br>10.28 | 270 (97), 192 (100) [$C_9H_6NS_2^+$] | 363, 459 | 8.65, 7.71, 7.62, 7.56, 7.24, 7.00, 6.96 | 155.0, 154.0, 152.1, 152.0, 149.6, 145.4, 136.6, 135.8, 124.2, 123.4, 121.5, 120.3, 118.2, 113.3 |

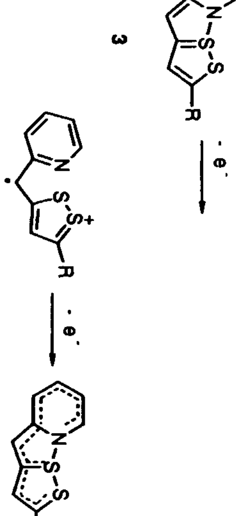
[a] Accompanied by the corresponding thiophene: [b] ca. 50%; [c] ca. 15%; [d] ca. 30%.

**Table II. Oxidation Potentials of Substituted (Pyridinylmethylidene)dithioles**

| compd no. | substituent | oxidation potential, V |
|---|---|---|
| **3a** | $n$-$C_4H_9$ | +0.75 |
| **3b** | 2-hydroxy-2-methylpropyl | +0.93 |
| **3c** | $C_6H_5$ | +0.70 |
| **3d** | 4-$CH_3C_6H_4$ | +0.73 |
| **3e** | 4-$CH_3OC_6H_4$ | +0.80 |
| **3f** | 2-$C_5H_4N$ | +0.86 |

The visible absorbance maxima of compounds **3** (409 nm for those containing aliphatic substituents to 458 nm for those with aromatic substituents) are consistent with those of the unsubstituted system **1** (414–480 nm).[1b,e] Annulation of a pyridine ring to the parent heteropentalene should result in a bathochromic shift of a least 30 nm from the unsubstituted system, and this shift has been demonstrated for naphthalene ($\lambda_{max}$ 221 nm) and anthracene ($\lambda_{max}$ 256 nm). Another interesting feature of their UV spectra is the similarity of the absorbance maxima of the three phenyl-substituted derivatives (**3c**, **3d**, and **3e**), all of which absorb at 442 nm. Normally a methyl group on a phenyl substituent produces a bathochromic shift of 10 nm and a methoxy group produces a bathochromic shift of 25 nm. These shifts do not occur in these cases, most likely the result of the non-coplanarity of the phenyl substituents with the parent ring, resulting in no $\pi$-orbital overlap (vide infra).

Oxidation potentials of **3** were determined by cyclic voltammetry in acetonitrile with tetraethylammonium tetrafluoroborate as the electrolyte. These are shown in Table II. All exhibited an irreversible oxidation which typically results from an unstable radical cation such as **8** undergoing a chemical reaction before it is reduced electrochemically. This phenomenon was independent of the scan rate. The three phenyl-substituted derivatives (**3c**, **3d**, and **3e**) showed two oxidations, one tentatively assigned as resulting from the oxidation to the radical-cation **8**, and the second from the oxidation of **8** to the dication **9**. Although there are many examples demonstrating[4] a correlation between Hammett $\sigma$ constants and oxidation potentials, none was observed in this series of heteropentalenes. We anticipated that a compound with strong electron-donating character such as **3e** would have a lower potential than a simple phenyl derivative **3c**, but this was not the case. This may be rationalized in terms of the lack of $\pi$-orbital overlap between the substituent and the parent ring, also suggested by the spectral data above.



**3** **8** **9**

It was not possible to assign an unambiguous structure to these azadithiapentalenes on the basis of spectral data. The single-crystal X-ray determination of **3a** is shown in Figure 1, and selected bond lengths and angles are listed in Table III. Particularly interesting features of this

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[4] Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967.

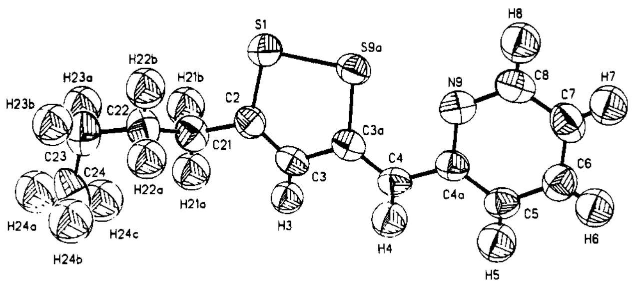


**Figure 1.** ORTEP representation of (pyridinylmethylidene)dithiole **3a**. (Atom numbers are for X-ray structural purposes only and are also used in Table III.)

**Table III. Selected Bond Lengths and Bond Angles[a] of 3a**

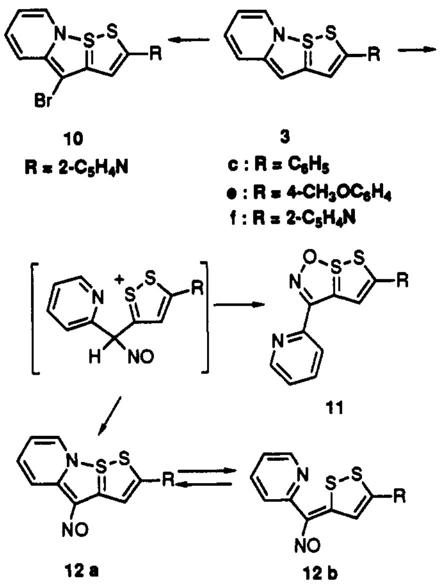
| | | bond length, Å | | | | angle, deg |
|---|---|---|---|---|---|---|
| S1 | S9a | 2.124 | S1 | S9a | N9 | 171.7 |
| S6a | N9 | 2.502 | S9a | S1 | C2 | 95.1 |
| C2 | C3 | 1.331 | S1 | S9a | C3a | 94.1 |
| C3 | C3a | 1.444 | S1 | C2 | C3 | 116.8 |
| C3a | C4 | 1.361 | C2 | C3 | C3a | 120.3 |
| C4 | C4a | 1.429 | S9a | C3a | C3 | 113.6 |
| | | | N9 | S9a | C3a | 77.5 |
| | | | S9a | C3a | C4 | 122.3 |
| | | | C3a | C4 | C4a | 122.6 |
| | | | C4 | C4a | N9 | 115.0 |
| | | | C4a | N9 | S9a | 102.5 |

[a] Numbering of atoms in Table III refers only to X-ray atoms labels used in Figure 1.

structure are the coplanarity of the pyridine and dithiole rings, the single-bond character for C3–C3a and C4–C4a (1.444 and 1.429 Å, respectively), and the double-bond character evident for C2–C3 and C3a–C4 (1.331 and 1.361 Å, respectively). The S–S bond length is appreciably shorter than those reported for the simple compound 1 (2.124 versus 2.435–2.497 Å). More importantly, the S–N bond length of 2.502 Å is well within the sum of the van der Waal radii for sulfur and nitrogen (3.35 Å) but is considerably longer than those found[5] for the simple compounds 1 (1.779–1.863 Å). The coplanarity of the molecule and the relatively short distance between the pyridine nitrogen and the sulfur atom of the dithiole clearly show their interaction. One may conclude that both the azadithiapentalene **3** and the dithiole form ***Z*-3′** contribute to the actual structure of these products and that neither form predominates. The lack of more bonding character between the sulfur and the nitrogen atom is most likely due to loss of aromaticity in the pyridine ring when a canonical form such as **3** is involved.

## Reactivity

Heteropentalenes have been reported[6] to undergo electrophilic substitution with a variety of reagents. Compound **3f** was brominated with 1 equiv of bromine in dichloromethane to furnish **10** (42%) for which a single-crystal X-ray structure was determined (supplementary material). A bathochromic shift of 12 nm in the UV spectrum of **10** is consistent with literature reports for the brominated products of **1**. Nitrosation of compounds **3c**, **3e**, and **3f** occurred at the same carbon to give, after a bond rotation and proton loss in the intermediate, the 5-aza-1,6a$\lambda^4$-dithia-6-oxapentalene **11**. The lack of a nitroso absorbance in the range of 500–600 nm in the visible spectrum of the nitrosated compounds is consistent with structure **11** as opposed to structure **12**.



**10**
**R = 2-C$_5$H$_4$N**

**3**
**c : R = C$_6$H$_5$**
**e : R = 4-CH$_3$OC$_6$H$_4$**
**f : R = 2-C$_5$H$_4$N**

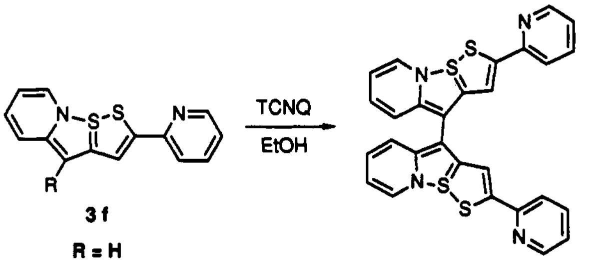
**11**

**12a** **12b**

Disulfides are reduced to dithiols by a variety of reducing agents, and compound **3f** was treated with several of these reagents. Tributylphosphine in methanol, tin or zinc in concentrated hydrochloric acid, and sodium borohydride in methanol had no effect on **3f** which was recovered unchanged.

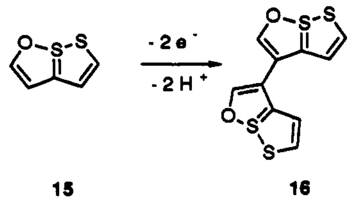
## Charge-Transfer Complexes

Reaction of **3** with organic electron acceptors in attempts to make charge-transfer complexes led to a mixture of compounds which was analyzed by high-pressure liquid chromatography and UV spectroscopy. An ethanol solution of **3f** and an ethanol solution of tetracyanoquinodimethane (TCNQ) resulted in an immediate dark-purple solution which after concentration of the solvent yielded black crystals amounting to 81% of the total weight of the two reactants. The decomposition point of these black crystals was 165 °C (cf. the melting point of **3f**, 213.5–214 °C and TCNQ, 287–289 °C). Separation provided a solid thought to be the dimer **14** based on the results of field desorption mass spectrometry (*m*/*z* 538). Pedersen has reported[7] an analogous reaction product **16** from the electrooxidation of the oxadithiapentalene **15**.



**3f**
**R = H**

**14**



**15** **16**

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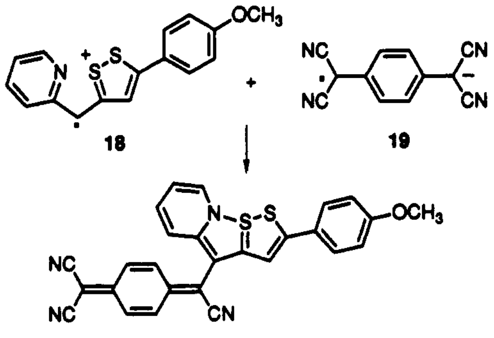
(5) Leung, F.; Nyburg, S. C. *Can. J. Chem.* **1972**, *50*, 324 and references listed therein.

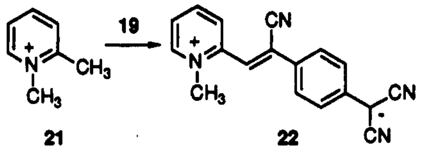
(6) (a) Beer, R. J. S.; Cartwright, D.; Harris, D. *Tetrahedron Lett.* **1967**, 953. (b) Beer, R. J. S.; Gait, R. J. *J. Chem. Soc., Chem. Commun.* **1970**, 328. (c) Duguay, G.; Reid, D. H.; Wade, K. O.; Webster, R. G. *J. Chem. Soc.* **1971**, 2829. (d) Christie, R. M.; Reid, D. H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 228.

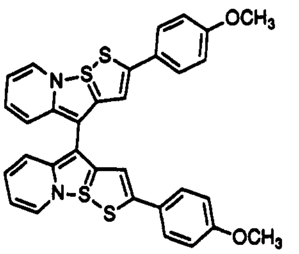
(7) Pedersen, C. Th.; Parker, V. D.; Hammerich, O. *Acta Chem. Scand.* **1976**, *B30*, 478.

Compound **3e** was reacted with TCNQ under similar conditions, resulting in a mixture of products separated by reverse-phase preparative liquid chromatography. The initial fraction was the TCNQ radical anion (perhaps with interaction of the acetonitrile used as solvent); fraction two eluted as a raspberry-colored solution which turned to a dark-purple solution on concentration and eventually to a dark-purple solid. The field desorption mass spectrum of this solid showed $m/z$ 476 which is consistent with structure **20**, formed by the coupling of compound **18** (the radical cation of **3e**) with the radical anion **19** of TCNQ with a subsequent loss of hydrogen cyanide. Precedence for this type of coupling is found in the work of Metzger and Heimer[8] who described the reaction of TCNQ radical anion with the pyridinium salt **21** to furnish the 1:1 adduct **22** formed as a result of the loss of 1 equiv of hydrogen cyanide. Fraction three was the starting material **3e** and fraction four was the dimer **23**. The structure of **23** is supported by a comparison of its $^1$H NMR spectrum with that of **3e** which showed the loss of the singlet at 7.09 ppm in an otherwise similar NMR spectrum.



**20**





**23**

Reaction of compounds **3** with the organic oxidizing agents 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and tetracyanoethylene (TCNE) provided products resulting from more than simple radical coupling of the oxidized species; the products had masses indicative of starting material or dimer plus the addition or loss of one or two sulfur atoms.

## Theoretical Considerations

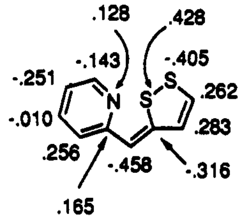
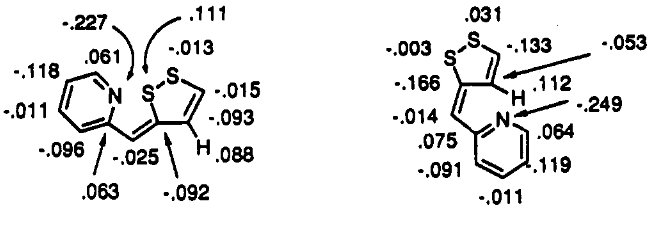


**Figure 2.** HOMO coefficients of the (pyridinylmethylidene)dithiole *Z*-3′.



Z - 3'                E - 3'

**Figure 3.** Charge densities of (pyridinylmethylidene)dithioles *Z*-3′ and *E*-3′.

The pyridoazadithiapentalenes **3** are likely to have electronic properties distinct from **1**, as the nitrogen atom is now part of what could be viewed as a separate aromatic nucleus. To study the effect of this environment on the S, N interaction and, in a more general sense, to evaluate the nature of this interaction, a series of molecular orbital calculations of **3** and **1** was carried out. The initial survey was performed using MNDO.[9] Although MNDO does not explicitly include d orbitals in the basis set, implicity the effects of these functions are included in the parameterization. The HOMO coefficients for compound **3** are shown in Figure 2. These data demonstrate the large amount of electron density in the $p_z$ orbital found on C4. This high charge density indicates that in an "orbital-controlled" reaction, substitution is likely to occur at that position, and the results of the electrophilic substitution reactions described above establishing C4 as the site of substitution are consistent with these calculations.

A comparison of ***Z*-3′** and ***E*-3′** yielded a small difference in energy (0.7 kcal mol$^{-1}$) for these two systems, with the *Z*-isomer preferred. A plot of charge densities for the compounds, as shown in Figure 3, reveals that most of the atoms in the two examples carry the same charge except for S6a and the hydrogen of C3. Each of these centers has a change in charge with the greater value found when the nitrogen is proximal. These observations suggest a stabilization of the *Z*-isomer via a polarization mechanism which outweighs the apparent coulombic mode of stabilization accorded the *E*-isomer. The details of this N, S interaction remain to be clarified, as MNDO clearly suggests the S, N interaction is not a formal bond, the bond order being a mere 0.009. Whether the interaction is a dative bond or falls into that category of bonds consistent with attractive interactions of the van der Waal's type[10] are issues not resolved at this level of theory.

MNDO was also used to examine the effect of a substituent on the parent system **3**. It was found in the event where the substituted phenyl was orthogonal to the parent ring system that the electron density in the $\pi$ orbitals, as indicated by the HOMO coefficients, is located in the main ring and not in the aryl substituent—this independent of the substituent on the phenyl ring (e.g., **3c**, **3f**, and R = 4-HOC$_6$H$_4$, 4-FC$_6$H$_4$, 2-O$_2$NC$_6$H$_4$, 4-C$_5$H$_4$N). It is known that MNDO favors the orthogonal arrangement for bonded aromatic systems, for example, the ring–ring dihedral angle in biphenyl is approximately equal to 90° according to MNDO. Thus it is not surprising to find that all the

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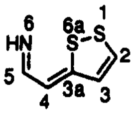
[8] Metzger, R. M.; Heimer, N. E. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 133.

[9] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

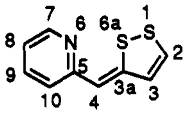
[10] Allinger, N. L.; Frierson, M.; Van-Catledge, F. A. *J. Am. Chem. Soc.* **1982**, *104*, 4592 and references listed therein.

**Table IV. Energies, Dipole Moments, Mulliken Charges, and Selected Distances for Azadithiapentalene and Its Isomers**



| | ***Z*-1′** | ***Z*-1′** | ***Z*-1″** | ***Z*-1″** | ***Z*-1″** | ***E*-1′** | ***E*-1″** |
|---|---|---|---|---|---|---|---|
| basis set | 3-21* | 6-31* | 3-21 | 3-21* | 6-31* | 3-21* | 3-21* |
| *E* (au) | −1036.597 808 | −1041.665 583 | −1036.389 719 | −1036.607 939 | −1041.658 616 | −1036.591 598 | −1036.594 143 |
| *n* (D) | 3.120 | 2.820 | 8.030 | 7.386 | 7.704 | 1.964 | 7.521 |
| S1 | 0.113 | 0.079 | −0.044 | −0.204 | −0.282 | 0.174 | −0.183 |
| C2 | −0.424 | −0.386 | −0.525 | −0.303 | −0.228 | −0.438 | −0.281 |
| C3 | −0.218 | −0.114 | −0.273 | −0.331 | −0.268 | −0.226 | −0.341 |
| C3a | −0.221 | −0.153 | −0.386 | −0.216 | −0.104 | −0.239 | −0.218 |
| C4 | −0.346 | −0.300 | −0.312 | −0.345 | −0.294 | −0.319 | −0.336 |
| C5 | 0.160 | 0.135 | 0.235 | 0.204 | 0.158 | 0.155 | 0.193 |
| N6 | −0.688 | −0.709 | −0.995 | −0.919 | −0.863 | −0.678 | −0.911 |
| S6a | 0.310 | 0.262 | 0.829 | 0.677 | 0.569 | 0.194 | 0.576 |
| $r_{S-S}$ | 2.109 | 2.092 | 2.951 | 2.898 | 2.951 | 2.080 | |
| $r_{N-S}$ | 2.592 | 2.809 | 1.784 | 1.720 | 1.718 | | 1.700 |

**Table V. Energies, Dipole Moments, Mulliken Charges, and Selected Distances for (*Z*)- and (*E*)-(Pyridinylmethylidene)dithiole**

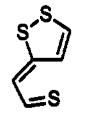


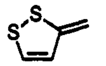
| | ***Z*-3′** | ***E*-3′** |
|---|---|---|
| basis set | 3-21* | 3-21* |
| *E* (au) | −1188.411 317 | −1188.405 264 |
| *n* (D) | 3.249 | 3.018 |
| S1 | 0.117 | 0.169 |
| C2 | −0.428 | −0.440 |
| C3 | −0.214 | −0.217 |
| C3a | −0.234 | −0.256 |
| C4 | −0.269 | −0.238 |
| C5 | 0.369 | 0.355 |
| N6 | −0.783 | −0.771 |
| S6a | 0.282 | 0.183 |
| C7 | 0.159 | 0.141 |
| C8 | −0.349 | −0.343 |
| C9 | −0.168 | −0.172 |
| C10 | −0.272 | −0.270 |
| $r_{S-S}$ | 2.106 | 2.081 |
| $r_{N-S}$ | 2.655 | |

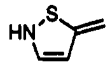
substituted phenyls in the (pyridinylmethylidene)dithioles were found by MNDO to be 88 ± 13° to the parent ring. Despite the inability to calculate trustworthy structures for the series, from the experimental observation of a relatively small effect of the aryl substituent on both the UV spectra and on the oxidation potential of the dithioles, coupled with the calculated HOMO, one can ascertain that the phenyl groups are not significantly conjugated (not coplanar) with the heterosystem.

Although these semiempirical results were appealing in that they agreed with chemical intuition, it was important to learn how a higher level of theory would describe systems 1 and 3. To that end ab initio studies of the compounds were carried out using Pople's GAUSSIAN program.[11] The results of these calculations are tabulated in Tables IV and V. In all cases the structures were completely optimized with the basis sets indicated. In the case of 1 calculated at the HF/6-31g* level, the two isomers 1′ and 1″ were also ascertained to be stationary points by calculating the vibrational spectrum of each. No stable point was found for the delocalized structure 1.

The pertinent point of the study was that in both systems 1 and 3 the stable structure was determined to be the dithiole form with a relatively weak interaction between the sulfur and nitrogen. The nature of this interaction appears to be independent to a large degree on whether the nitrogen is an imine-type or in a pyridine ring. The difference in energy between the isomer having the sulfur and nitrogen adjacent, ***Z*-1′** or ***Z*-3′**, and that isomer where the interaction would be absent (***E*-1′** or ***E*-3′**) is in the case of 1′, 3.9 kcal mol$^{-1}$ and for 3′, 3.8 kcal mol$^{-1}$. As in the above MNDO results, the charge distribution hints at what is occurring. The S–S bond in isomer ***E*-1′** or ***E*-3′** is relatively unpolarized, the difference in Mulliken charges for the sulfurs being 0.020 and 0.014 electrons, while in the corresponding *Z*-isomers, the S–S bond is distinctly polarized, the difference in charges on the two sulfurs being equal to 0.197 and 0.165 electrons, respectively. Additionally, as in the semiempirical cases the hydrogen of C3 reflects in each case the corresponding change in charge of S6a. The dithiole portion of system 1 or 3 was, based on geometric considerations, only slightly perturbed from the calculated geometry of the model methylenedithiole 24 (Table VI).


**2′**


**24**


**25**

A survey of the literature indicated that optimized structures had not been obtained for the azadithiapentalenes and that the highest quality calculations were single-point determinations on experimental geometries.[12] In that work, Palmer and Findlay had deduced that the interaction of the sulfur and nitrogen was likely to be a weak one, and of the heteropentalene series the "parent" trithiapentalene 2 had the strongest bond between the sulfur atoms. For 2, a symmetric structure was assumed based on experimental data. Since there was little doubt from both experimental and theoretical studies of 2 that the symmetric configuration is the minimum energy form and that the S–S interaction is a strong one, we carried out a cursory investigation of trithiapentalene (Table VI) to compare the strong interaction case with our weakly-bonded one. The system was fully optimized at the

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[11] Frisch, M. J.; Binkley, J. S.; Schegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *GAUSSIAN 86*; Carnegie-Mellon University: Pittsburgh, 1984.

[12] Palmer, M. H.; Findlay, R. H. *J. Chem. Soc., Perkin Trans. 2* 1974, 1885.

**Table VI. Energies, Dipole Moments, Mulliken Charges, and Selected Distances for Trithiapentalene and Reference Structures**[a]

| | 2 | 2 | *Z*-2′ | 24 | 24 | 25 |
|---|---|---|---|---|---|---|
| basis set | 3G | 3-21* | 3-21* | 3G | 3-21* | 3-21* |
| *E* (au) | −1368.773 557<br>−1368.771 484[b] | −1377.536 783 | −1377.550 691 | −938.256 338 | −944.232 485 | −603.274 034 |
| $\mu$ (D) | 1.547 | 3.908 | 5.163 | 1.055 | 2.268 | 2.278 |
| S1 | 0.009 | −0.004 | 0.180 | 0.115 | 0.165 | |
| C2 | −0.140 | −0.349 | −0.425 | −0.161 | −0.436 | |
| C3 | −0.132 | −0.273 | −0.215 | −0.086 | −0.204 | −0.465 |
| C3a | −0.050 | −0.216 | −0.239 | −0.085 | −0.282 | −0.268 |
| C4 | −0.132 | −0.273 | −0.306 | −0.160 | −0.433 | −0.307 |
| C5 | −0.140 | −0.349 | −0.313 | | | 0.114 |
| S6 | 0.009 | −0.004 | −0.085 | | | −0.864 (N6) |
| S6a | 0.295 | 0.379 | 0.325 | 0.105 | 0.181 | 0.475 |
| $r_{S1-S6a}$ | 2.320 | 2.403 | 2.094 | 2.089 | 2.090 | $r_{S-N}$ = 1.726 |
| $r_{S6a-S6}$ | | | 3.020 | | | |

[a] Atom labels are the same as in Tables IV and V. [b] Reference 13.

HF/3-21g* level and was found to prefer the dithiole, unsymmetric form **2′**, by 8.7 kcal mol$^{-1}$ over symmetric structure **2**. A review of the literature indicates that in previous studies[13] of this system with ab initio methods, the symmetric form was imposed and complete optimization of the molecule had not been done. Although additional studies of the systems are necessary, given the difficulties in obtaining accurate descriptions of molecules containing second-row elements at the simple Hartree–Fock level, our initial conclusions from all these calculations is that an accurate representation of the heteropentalenes is not to be obtained by a single Hartree–Fock determinant. Furthermore, the possibility that these systems are examples of sulfur in a hypervalent bonding arrangement needs additional investigation using a multiconfiguration representation.[14]

## Experimental Section[15]

**General.** The pyridinyl-substituted butadiynes **3** were prepared as reported.[3] 1,4-Diphenylbuta-1,3-diyne was generously provided by Dr. D. M. White of General Electric Co. 1,4-Di(4-pyridinyl)buta-1,3-diyne was synthesized as reported.[11] Other starting materials and solvents were commercial products. *Reactions performed with gaseous hydrogen sulfide were run with sodium hydroxide and Clorox traps at the outlet of the reaction flask.*

**General Procedure for the Addition of Hydrogen Sulfide to Pyridinylbutadiynes. The Preparation of (Pyridinylmethylidene)dithioles 3.** Gaseous $H_2S$ was bubbled into a solution of 1-(2-pyridinyl)octa-1,3-diyne (**4a**) (0.43 g, 2.35 mmol) and sodium hydroxide (0.20 g, 5.0 mmol) in methanol (75 mL) at room temperature for 2.5 h. The reaction mixture was stirred for 15 h at room temperature and then filtered to remove the orange precipitate that had formed. The crude solid was purified by column chromatography (silica gel, hexane–ethyl acetate) yielding the **3a** as orange microneedles: 38%, mp 63–64 °C (Table I).

**Preparation of 2,5-Diphenylthiophene (5a).** Gaseous $H_2S$ was bubbled into a solution of 1,4-diphenylbuta-1,3-diyne (**6a**) (10.1 g, 50 mmol) and sodium hydroxide (4.0 g, 100 mmol) in methanol (150 mL) at room temperature for 3 h. The reaction mixture was stirred for 15 h under reflux, and after cooling, a UV–visible spectral analysis of the crude reaction mixture showed only absorbances for the starting butadiyne and thiophene (325 nm; reported[16] UV max 323 nm in heptane). There was no indication of the desired 1,2-dithiole at 400 nm. High-pressure liquid chromatography indicated the presence of starting material and one other product.

**Preparation of 2,5-Di(4-pyridinyl)thiophene (5b).** Gaseous $H_2S$ was bubbled into a solution of 1,4-di(4-pyridinyl)buta-1,3-diyne (**6b**) (95 mg, 0.46 mmol) and sodium hydroxide (55 mg, 1.48 mmol) in methanol (6 mL) at room temperature for 1 h. The reaction mixture stirred at room temperature for 15 h. The homogeneous reaction mixture was added to $H_2O$ (3 mL) and extracted with $CH_2Cl_2$ (3 × 2 mL). Evaporation of the combined organic layers provided a light yellow solid: 109 mg (100% crude thiophene; UV max 362 nm); mpt 172–174 °C; IR (KBr) 1575, 813, 795, 685 nm; $^1$H NMR ($CDCl_3$/DMSO-$d_6$) $\delta$ 8.63 (d, 4 H, *J* = 6.0 Hz), 7.53 (s, 2 H), 7.50 (d, 4 H, *J* = 6.0 Hz). The crude material was not purified further.

**Bromination of (Pyridinylmethylidene)dithiole 3f To Form 10.** A solution of **3f** (32.4 mg, 0.12 mmol) in dichloromethane (1.5 mL) was stirred with bromine (19 mg, 0.12 mmol) at room temperature for 5 min. The reaction mixture was then washed with NaOH solution and extracted with $CH_2Cl_2$ (3 × 1 mL). The combined organic extracts were concentrated in vacuo to a dark solid that was purified by column chromatography (silica gel, hexane–ethyl acetate), yielding **10** as yellow irregular prisms: 17.7 mg (42%), mp 115 °C dec; IR (KBr) 1590, 1460, 845, 800 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 8.68 (d, 1 H, $H_6$, $J_{6,5}$ = 4.8 Hz), 8.62 (d, 1 H, $H_6$, $J_{6,5}$ = 4.6 Hz), 8.06 (s, 1 H, vinylic), 7.73–7.86 (m, 4 H, aromatic), 7.31 (t, 1 H, aromatic, *J* = 5.2 Hz), 7.11 (t, 1 H, aromatic, *J* = 5.2 Hz); UV ($CH_3OH$) nm 472; MS *m/z* (relative intensity) 350, 348 [M$^+$] (100), 269 [M$^+$ − Br] (66), 205 [M$^+$ − Br − 2S] (28), 149 (41).

**General Procedure for the Nitrosation of (Pyridinylmethylidene)dithioles. The Preparation of Pyridinyl-Substituted 5-Aza-1,6a$\lambda^4$-dithia-6-oxapentalene (11).** A solution of **3** in acetonitrile–acetic acid (1:1) was treated with 2 equiv of sodium nitrite. The initially heterogeneous mixture became homogeneous and dark red in color. After being stirred for 10

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(13) Nyberg, S. C.; Theodorakopoulous, G.; Csizmadia, I. G. *Theoret. Chim. Acta (Berlin)* 1977, *45*, 21.

(14) (a) Messmer, R.; Patterson, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 4138. (b) During the time this manuscript was in preparation, a report appeared (Cimiraglia, R.; Hofmann, H.-J. *J. Am. Chem. Soc.* **1991**, *113*, 6449) in which these authors, as suggested by us, found that the symmetric structure was obtained for **2** when one includes correlation.

(15) Spectral characteristics were carried out on the following instrumentation: $^1$H NMR spectra, Varian EM 390 spectrometer using $CDCl_3$ as solvent; $^{13}$C NMR spectra (50.3 MHz) with proton decoupling, Varian XL-200 spectrometer chemical shifts being reported in $\delta$ (parts per million) downfield from tetrmethylsilane ($\delta$ 0.00) as an internal standard; IR spectra, Perkin-Elmer 598 spectrophotometer as KBr pellets; ultraviolet–visible spectra, Shimadzu UV-240 spectrophotometer using methanol as solvent; mass spectra (MS) and high-resolution mass spectra (HRMS), MAT 731 high-resolution double-focusing mass spectrometer using electron impact at 70 eV, respectively. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Oxidation potentials were determined by cyclic voltammetry on a Bioanalytical Systems, Inc., Electroanalytical Instrument Model CV-27 cyclic voltammograph using dichloromethane as the solvent and tetraethylammonium tetrafluoroborate as the electrolyte. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, TN. High-pressure liquid chromatographic analytical separations were carried out on a Shimadzu Model LC4A liquid chromatograph using a Dupont $C_{19}$ column, and preparative separations were performed using E. M. Merck silica gel (0.063–0.200 mm) in Michel-Miller columns with a fluid metering piston-driven pump and an ISCO Model UA-5 detector.

(16) Kutsyna, L. M.; Sidorova, R. P.; Voevoda, L. V.; Ishchenko, I. K.; Demchenko, N. P.; *Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl)* **1962**, *26*, 1322.

min at room temperature, the reaction mixture was washed with $NaHCO_3$ solution and extracted with $CH_2Cl_2$. Evaporation of the $CH_2Cl_2$ gave a crude product that was purified by chromatography (silica gel, hexane–ethyl acetate), providing **11** as orange-red, irregular prisms. **11a** (69%): mp 121.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 9.85 (s, 1 H, aromatic), 8.82 (s, 1 H, aromatic), 8.27 (d, 1 H, aromatic, $J$ = 8.1 Hz), 7.90 (m, 3 H, aromatic), 7.52 (m, 3 H, aromatic), 7.42 (dd, 1 H, aromatic, $J$ = 1.9 Hz, $J$ = 5.5 Hz); UV ($CH_3CN$) nm (log $\epsilon$) 422 (3.96), 320 (3.94), 293 (4.01); high-resolution mass spectra, experimental $m/z$ 298.0223 (calcd $m/z$ 298.0234). **11b** (40%): mp 164 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 9.76 (s, 1 H, aromatic), 8.85 (br s, 1 H, aromatic), 8.26 (br s, 1 H, aromatic), 7.91 (d, 2 H, aromatic, $J$ = 8.7 Hz), 7.88 (m, 1 H, aromatic), 7.41 (br s, 1 H, aromatic), 7.01 (d, 2 H, aromatic, $J$ = 8.7 Hz), 3.90 (s, 3 H, $ArOCH_3$); UV ($CH_3CN$) nm (log $\epsilon$) 429 (4.29), 352 (4.07), 239 (4.55); high-resolution mass spectra, experimental $m/z$ 328.0342 (calcd $m/z$ 328.0340). **11c** (70%): mp 182–184 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 10.15 (s, 1 H, aromatic), 8.86 (d, 1 H, aromatic, $J_{6,5}$ = 4.4 Hz), 8.78 (dd, 1 H, aromatic, $J_{6,4}$ = 1.3 Hz, $J_{6,5}$ = 4.8 Hz), 8.25 (d, 1 H, aromatic, $J$ = 8.05 Hz), 8.05 (d, 1 H, aromatic, $J$ = 7.4 Hz), 7.88 (m, 2 H, aromatic), 7.42 (m, 2 H, aromatic); UV ($CH_3CN$) nm (log $\epsilon$) 428 (3.56), 318 (3.62), 265 (3.64); high-resolution mass spectra, experimental $m/z$ 299.0194 (calcd $m/z$ 299.0187).

**Dimer 14 of Compound 3f.** 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (42 mg, 0.185 mmol) was added to a solution of **3f** (50 mg, 0.185 mmol) in acetonitrile (2 mL). The solution was concentrated to half volume, and upon cooling, a dark solid was collected by filtration and then dried in vacuo. The crude product was purified by column chromatography (silica gel, hexane–ethyl acetate) to provide a red solid: 55 mg; field desorption mass spectrum, $m/z$ 538.

**Oxidation of Compound 3e with TCNQ.** A hot solution of tetracyanoquinodimethane (5.3 mg, 0.026 mmol) in acetonitrile (1.5 mL) was added to a hot solution of **3e** (7.7 mg, 0.026 mmol) in acetonitrile (1.5 mL). The dark reaction mixture was concentrated to half volume, and after cooling, no precipitate had formed. Evaporation to dryness yielded a residue that on analysis by field desorption mass spectrometry was shown to be a mixture of products other than starting materials. Purification by column chromatography (silica-$C_{18}$, water–acetonitrile) of this residue provided several fractions. First fraction: **TCNQ-radical anion**[17] **19**; 5.1 mg; UV ($CH_3CN$) nm 840, 721; in acid 395 nm (TCNQ). Second fraction: 1:1 **adduct 20**; 1.6 mg (13%); UV ($CH_3CN$) nm 550, 318; high-resolution mass spectra, experimental $m/z$ 476.0765 (calcd $m/z$ 476.0766). Third fraction: **3e**; 4.5 mg (58% recovery of starting material); UV ($CH_3CN$) nm 442, 308. Fourth fraction: **dimer 23**; 1.4 mg (18%); UV ($CH_3CN$) nm 460, 312; EI mass spectrum 596 ($M^+$), 532 [$M^+$ – 2S], 531, 431.

**Acknowledgment.** We express our appreciation to Dr. R. Kullnig for the determination of the single-crystal X-ray structures.

**Registry No.** **3a**, 141511-37-7; **3b**, 141511-38-8; **3c**, 141526-51-4; **3d**, 141511-39-9; **3e**, 141511-40-2; **3f**, 141511-41-3; **4a**, 141511-35-5; **4b**, 141511-36-6; **4c**, 117635-47-9; **4d**, 117635-48-0; **4e**, 22779-13-1; **4f**, 29768-12-5; **5a**, 1445-78-9; **5b**, 141511-42-4; **6a**, 886-66-8; **6b**, 91508-53-1; **10**, 141511-43-5; **11a**, 141511-44-6; **11b**, 141511-45-7; **11c**, 141511-46-8; **14**, 141511-47-9; **19**, 34507-61-4; **20**, 141511-49-1; **23**, 141511-48-0.

**Supplementary Material Available:** Tables of atomic coordinates, bond distances and bond angles, and anisotropic thermal parameters for (pyridinylmethylidene)dithiole **3a** and also for **10**, the bromination product of **3f**, Z-matrices of optimized structures, a table of calculated frequencies for ***Z*-1′**, ***Z*-1″**, and NMR spectral data for compounds **3b**, **3d**, and **10** (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[17] Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.

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# Synthesis and Stereochemical Assignment of Heterocycles Derived from (2*S**,2′*S**,4*R**,4′*R**,6*S**,6′*S**)-4,4′,6,6′-Tetramethylperhydro-2,2′-bipyrimidine

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(2*S**,2′*S**,4*R**,4′*R**,6*S**,6′*S**)-4,4′,6,6′-Tetramethylperhydro-2,2′-bipyrimidine (**1**) reacts with excess formaldehyde in MeOH to give predominantly the tetracycle (1*R**,3*S**,5*R**,7*S**,8b*S**,8c*S**)-1,3,5,7-tetramethylperhydro-3a,4a,7a,8a-tetraazacyclopentano[*def*]fluorene (**2**) and in $Et_2O$ to give exclusively tetracycle (1*R**,3*S**,5*S**,7*R**,8b*S**,8c*S**)-1,3,5,7-tetramethylperhydro-3a,4a,7a,8a-tetraazacyclopentano[*def*]fluorene (**3**). With less formaldehyde, compound **1** yields an unusual 1:5 mixture of trans and cis tricycles, (1*R**,3S*,4a*S**,4b*S**,6*S**,8*R**)-1,3,6,8-tetramethylperhydro-4,5,8a,9a-tetraazafluorene (**5**) and (1*R**,3*S**,4a*S**,4b*S**,6*R**,8*S**)-1,3,6,8-tetramethylperhydro-4,5,8a,9a-tetraazafluorene (**6**), respectively, in MeOH solvent but gives almost exclusively the trans tricycle **5** in $Et_2O$. The structure of tetracycle **2** is supported by X-ray crystallographic data. Compounds **3** and **6** represent new structural types, and they appear to be conformationally stable. A mechanistic scheme for the formation of the tricycles and tetracycles which is consistent with the observed stereochemical changes is proposed.

## Introduction

The condensation of 1,3-alkanediamines with glyoxal was rediscovered recently as a convenient route to perhydro-2,2′-bipyrimidines [2,2′-bis(hexahydropyrimidines].[1] X-ray crystallographic analysis has since provided the first unambiguous proof of the molecular structure of perhydrobipyrimidines as their free amines,[2] and $^{13}C$ NMR data have been used to support the presence of similar structures in solution.[3] Subsequent conversion of perhydrobipyrimidines into perhydro-4,5,8a,9a-tetraazafluorenes and perhydro-3a,4a,7a,8a-tetraazacyclopentano[*def*]fluorenes has also been demonstrated in relatively simple cases.[1] The latter

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[1] Black, D. StC.; Craig, D. C.; Giitsidis, O.; Read, R. W.; Salek, A.; Sefton, M. A. *J. Org. Chem.* **1989**, *54*, 4771.

[2] Black, D. StC.; Craig, D. C.; Kassiou, M.; Read, R. W. *Aust. J. Chem.* **1991**, *44*, 143.

[3] Black, D. StC.; Kassiou, M.; Read, R. W. *J. Org. Chem.* **1991**, *56*, 4308.

0022-3263/92/1957-3901$03.00/0