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Electronic Structure of Heterospirenes—PE Spectroscopic Investigations

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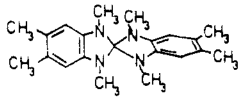
The synthesis of the heterospirenes **1**–**9** is described and their He I photoelectron (PE) spectra are recorded. The assignment of the first PE bands is based on a comparison with fragment molecules and on molecular orbital calculations using semiempirical methods (PPP, MINDO/3). In the case of **1**, **2**, **4**, and **5** strong spirointeraction has been elucidated. For **3** the analysis of the spectrum is hampered due to the strong overlap of bands while for **6** the nonplanarity brings about a reduction of spirointeractions. For **7**–**9** the interaction between both fragments could not be detected.

The linkage of two cyclic systems by a central sp^3-hybridized atom (C, Si, etc.) gives rise to spirocompounds. If both ring fragments consist of conjugated π-electron systems, then one is dealing with the spiropolyenes or spirenes. Despite their mutually perpendicular π-electron systems, both ring fragments are capable of interacting with each other.[1,2] This interaction has been called spiroconjugation.[1-3]

In the last 15 years several investigations using photoelectron (PE)[3-5] and electron spectroscopy[1,3,5c,6] have been published which give evidence for spiroconjugation. In this paper we report on our PE-spectroscopic investigations of the heterocyclic π-systems **1**–**6** built up of two equal fragments and of the heterocycles **7**–**9** composed of two different moieties. This work has been carried out in connection with our earlier PE investigations on **10**–**14**.[4]



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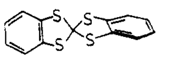

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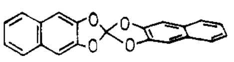

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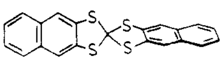

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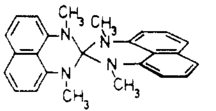

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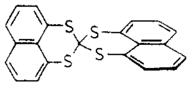

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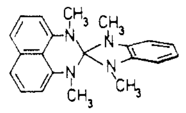

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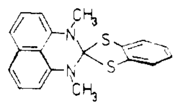

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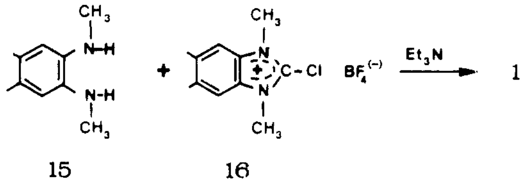
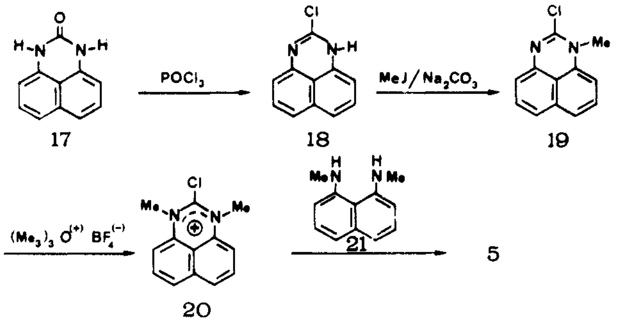
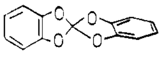
Scheme I



Scheme II





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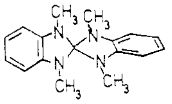

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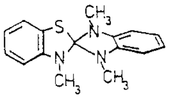

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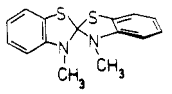

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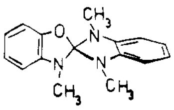

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Synthesis. The heterocyclic spiro compounds investigated in this paper are O, N, and S functional orthocarbonic acid derivatives. The synthesis of such compounds has been reviewed on several occasions.[3,7] The synthesis of **1**, **5**, **7**, and **8** was achieved analogously to the approach of Quast and Schmitt.[8] In Schemes I and II we show as examples the synthesis of **1** and **5**. Spirocompound **1** is prepared from 4,5,*N*,*N'*-tetramethyl-*o*-phenylenediamine (**15**) and 2-chloro-1,3,5,6-tetramethylbenzimidazolium tetrafluoroborate (**16**). The starting point for

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[1] Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208.

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[5] (a) Schweig, A.; Weidner, U.; Hellwinkel, H.; Knapp, W. *Angew. Chem.* **1973**, *85*, 360, *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 310. (b) Schweig, A.; Weidner, U.; Hill, R. K.; Cullison, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 5426. (c) Batich, C.; Heilbronner, E.; Rommel, E.; Semmelhack, M. F.; Foos, J. S. *J. Am. Chem. Soc.* **1974**, *96*, 7662. (d) Bischof, P.; Gleiter, R.; Dürr, R.; Ruge, B.; Herbst, P. *Chem. Ber.* **1976**, *109*, 1412. (e) Kobayashi, M.; Gleiter, R.; Coffen, D. L.; Bock, H.; Schulz, W.; Stein, H. *Tetrahedron* **1977**, *33*, 433. (f) Baker, A. D.; Bisk, M. A.; Venanzi, T. S.; Kwon, Y. S.; Sadha, S.; Liotta, D. C. *Tetrahedron Lett.* **1976**, 3415.

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[8] Quast, H.; Schmitt, E. *Chem. Ber.* **1968**, *101*, 1137.

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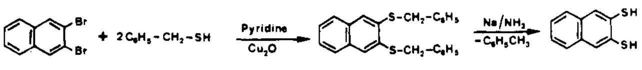
Scheme III



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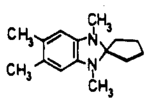
the preparation of **5** was perimidone **17**, which was prepared from the diamine and urea.[9] Compound **17** was transformed into the 2-chloro-1*H*-perimidine (**18**) by treating with $POCl_3$.[9,10] After methylation with methyl iodide (to yield **19**), followed by treatment with trimethyloxonium tetrafluoroborate, the dimethyl product **20** was obtained. The latter was reacted with *N,N′*-dimethylnaphthalene-1,8-diamine (**21**)[11] to yield **5**.

For further help in elucidating spirointeractions, we also prepared the cyclic diamines **22**,[12] **23**,[13] **24**,[14] and **25** by reaction of the corresponding amine with the appropriate carbonyl compound.



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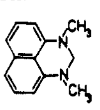

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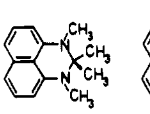

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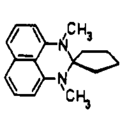

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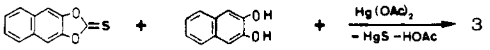
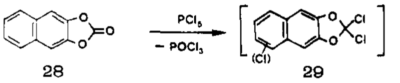
To prepare **3** we reacted the thiocarbonate **26** with naphthalene-2,3-diol (**27**) and Hg $(OAc)_2$ in tetrahydrofuran, modifying a general method for the hydrolysis of thiocarbonates[15] according to (1). Despite its somewhat low yield (20%) the reaction proved to be quite useful due to the ready availability of the starting materials.



(1)

26 27

The alternative route[16] to **3** via chlorination of the carbonate **28** with PCl_5 and subsequent reaction with **27** proved to be less favorable. Besides **3**, which was obtained in very low yield, we obtained a chlorinated derivative of **3** (**30**). To estimate the spirointeraction of **3** we used naphtho[2,3-*d*]-1,3-dioxole (**31**)[17] as a reference compound.



(2a)

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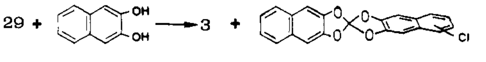
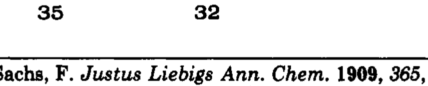


(2b)

27 30

For the preparation of the spirocompounds with sulfur as heteroatoms (**2**, **4**, and **6**), we applied the transesterification reaction of the corresponding dithiols with tetramethyl orthothiocarbonate (**32**).[18] The preparation of benzene-1,2-dithiol (**33**)[19] and naphthalene-1,8-dithiol (**34**)[20] was achieved according to the literature. Naphthalene-2,3-dithiol (**35**) was prepared according to a general method described by Adams et al.[21] Starting from 2,3-dibromonaphthalene (**36**) we obtained **35** via 2,3-bis(benzylthio)naphthalene (**38**) according to Scheme III. The preparation of the fragment molecules **39**–**41** was achieved by reaction of the corresponding dithiols with acetone.



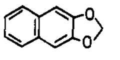
(3)

35 32

Table I. Measured Vertical Ionization Energies ($I_{v,j}$, eV) and Calculated Orbital Energies (ϵ_j) of 1, 2, 22, and 39

compd	band	$I_{v,j}$	assignment	$-\epsilon_j$ PPP	$-\epsilon_j$ MINDO/3
1	1 2	6.45	13 e[b]	6.79	7.27[a]
	3	7.4	3 a_2	7.65	8.30
	4	7.9	3 b_1	8.24	8.55
	5		12 e	9.77	9.77
	6	9.3			
	7		2 a_2	9.89	10.59
	8	9.8	2 b_1	10.68	11.17
2	1 2	7.85	10 e[c]	7.50	8.00
	3	8.29	2 a_2	7.94	8.48
	4	8.92	2 b_1	8.56	9.15
	5	9.92	1 a_2	9.57	10.02
	6		9 e	9.88	11.08
	7	10.3			
	8		1 b_1	10.17	11.47
22	1	6.35	5 b_1[d]	6.07	7.15[e]
	2	7.6	3 a_2	7.33	8.41
	3	9.0	4 b_1	9.28	9.80
	4	9.45	2 a_2	9.59	10.85
39	1	7.66	6 b_1[c]	7.36	8.07
	2	8.33	3 a_2	8.18	8.68
	3	9.77	2 a_2	9.86	10.10
	4	10.18	5 b_1	9.68	10.39
	5	10.9	7 $b_2(\sigma)$		8.78

[a] The calculations refer to **42**. [b] The numbers refer to the valence orbitals of **42**. [c] The numbers refer to the valence orbitals only. [d] The numbers refer to **43**. [e] The calculations refer to **43**.



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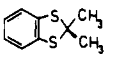

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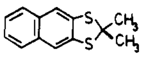

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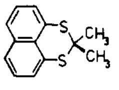

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PE Spectra of 1 and 2. The PE spectra of **1** and **2** are shown in Figure 1. Both show a relatively broad band at the low energy side of the spectrum, followed by two sharp peaks (bands 3 and 4). At higher energies a broad peak (bands 5–7) is clearly separated from the region of the strongly overlapping bands. To estimate the interactions prevailing in **1** and **2** we also recorded the PE spectra of **22** and **39**. Both spectra (Figure 1) show several peaks clearly separated from the area of strongly overlapping bands at higher energies. To assign the PE spectra of **1**, **2**, **22**, and **39**, we assume that the measured vertical ionization energies, I_{vj}, can be set equal to the negative value of the calculated orbital energies, $-\epsilon_j$ (Koopmans' theorem[22]) (Table I).

Using semiempirical methods (e.g., PPP,[23] MINDO/3[24])

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(9) Sachs, F. *Justus Liebigs Ann. Chem.* **1909**, *365*, 135.

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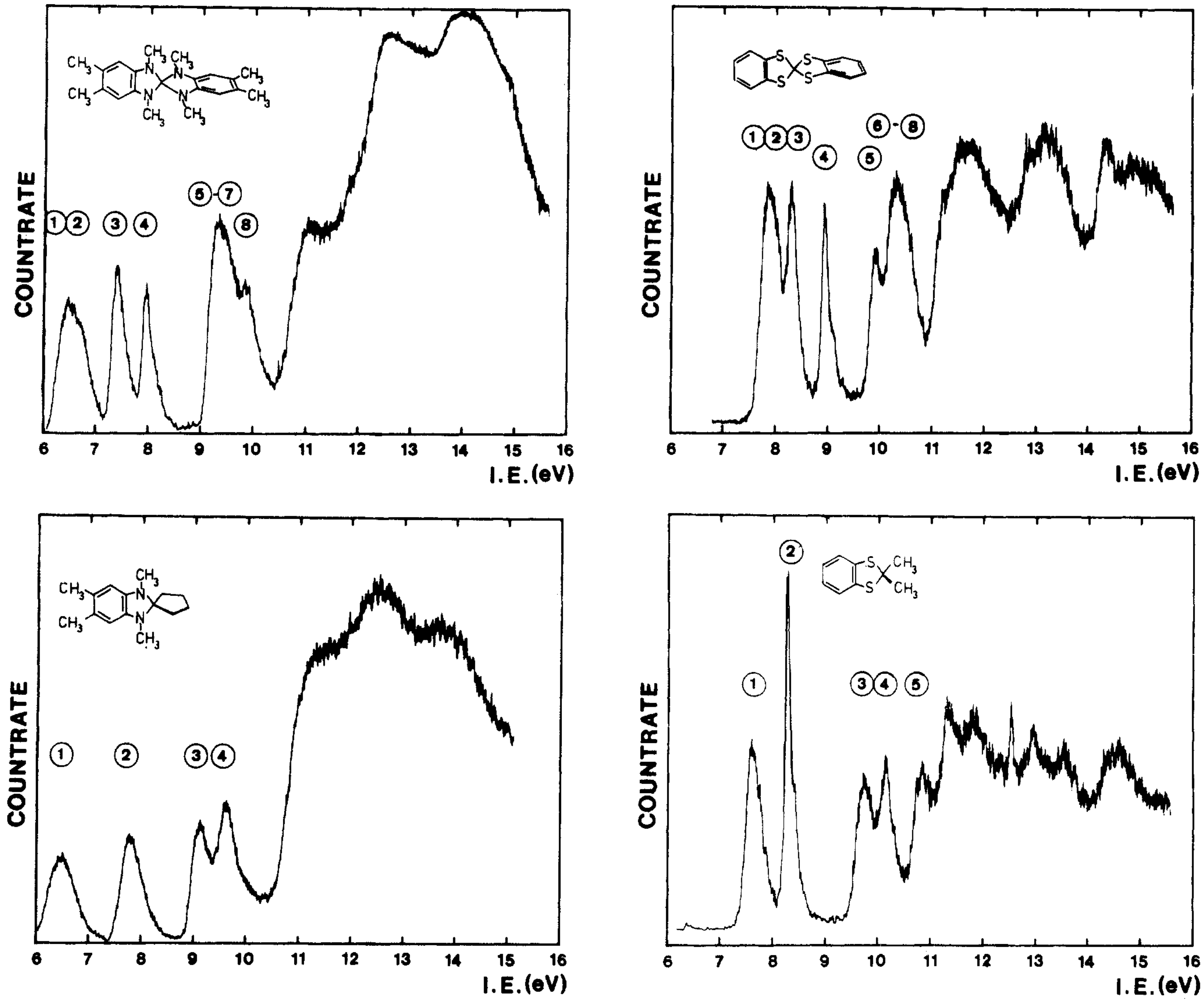
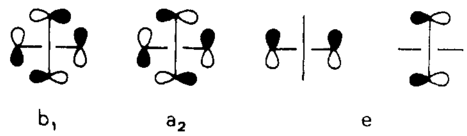


Figure 1. PE spectra of 1, 2, 22, and 39.

and adopting standard parameters for the PPP method,[26] we obtain for the highest occupied π-MO's of **22** and **39** wave functions which are symmetric (B_1) and antisymmeric (A_2) with respect to a plane of symmetry perpendicular to the molecular plane. The orbital sequence and a schematic drawing of the wave functions are shown on the left of Figure 2. The general features of this figure agree with the results of earlier investigations of *o*-phenylenediamine derivatives.[4,12]

Joining the two π-fragments of **22** or **39** together via a sp^3 carbon center yields **1** and **2**, respectively. In the resulting spirocompounds only those π-MO's belonging to the irreducible representation A_2 will interact with each other, while the symmetric MO's (B_1) will remain unchanged.

The reason for this can best be seen if we consider the Newman projections of the corresponding atomic orbitals at those centers which are connected with the central carbon atom. It can be clearly seen that only the antisymmetric wave functions find a partner from the other fragment which can give rise to an "in phase" (B_1) or an "out phase" (A_2) linear combination while the symmetric MO's of one fragment will remain unchanged and contribute to the E wave functions. On the right side of Figure 2 the corresponding interaction diagram is shown for the spirocompounds.



This diagram also leads to an empirical interpretation of the PE spectra of **1** and **2** via comparison of the spectrum of **1** with that of **22** and of **2** with that of **39**. In Figure 3 the first levels in the spectra of **1** and **2** are compared with those of **22** and **39**, the former two being shifted by 0.2 eV to higher energy. This shift seems reasonable due to the inductive effect of the additional heteroatoms in the spirocompounds. The comparison of the related spectra suggests that the first peak in the spectra of **1** and **2** should be assigned to ionizations out of the e MO's. The splittings between bands 3 and 4 in the PE spectra of **1** and **2** are caused by spirointeractions. The assignment of bands 5 to 8 in the spectra of the spirocompounds is less straightforward as the previous ones due to the substantial overlap of these bands. The suggested assignment in Figure 3 is based on a reversed sequence of bands 3 and 4 of **39** relative to the sequence in **22**.

The proposed assignment of bands 1 to 8 (see Figure 3) for **1** and **2** is in agreement with relative intensity considerations. The first peak (bands 1 and 2) in the PE spectra of both spirocompounds is approximately twice as

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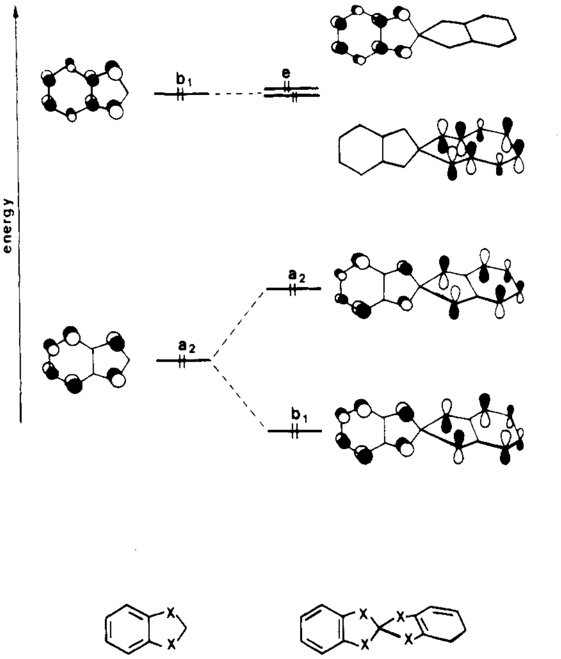


Figure 2. Schematic correlation between the highest occupied π-orbitals of compounds of the type **22** or **39** with the corresponding spirocompounds.

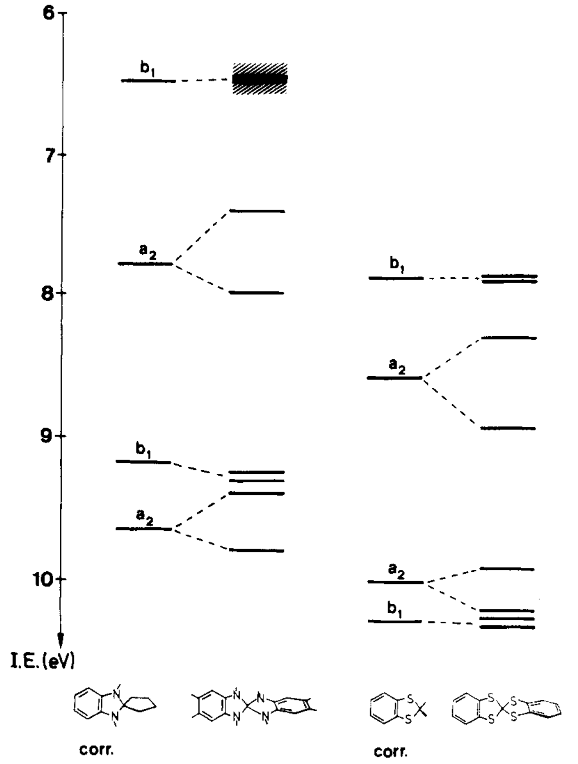
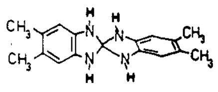


Figure 3. Comparison between the first bands of the PE spectra of **22** and **39**, corrected for the substituent effects, with those of **1** and **2**.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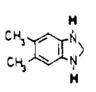
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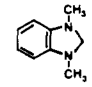
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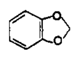
45

intense as are bands 3 and 4. Similarly, the peak for 5–7 in the PE spectrum of **1** is about three times the size of band 8 and a similar ratio is found if we compare bands 6–8 in the PE spectrum of **2** with band 5. To aid our assignments we have carried out MO calculations on **42** and **43**, as models for **1** and **22** respectively, as well as on **2** and **39**. For these calculations we applied the PPP[23] and the MINDO/3[24] methods. For the PPP calculations the parameters recommended by Fabian, Mehlhorn, and Zahradnik[26] (see also Experimental Section) were used. Since the geometries of **1** and **2** as well as of the corresponding model compounds were unknown, we have calculated them by varying all geometrical parameters with respect to the heat of formation using the MINDO/3 procedure. The orbital energies listed in Table I are based on these results.

The orbital sequence obtained by both of the semiempirical methods confirms the empirical assignments for bands 1–4 just discussed. These calculations suggest that the split between the fourth and fifth peaks in the PE spectra of **1** and **2** is also brought about by spirointeraction.

The resonance integrals, β_{spiro}, between the two perpendicular π-fragments have been calculated by using two different approaches. Using the PPP method we have varied the value of β_{spiro} for **1** and **2** until the calculated split between the orbitals a_2 and b_1 was equal to the split between bands 3 and 4 in the PE spectra of **1** and **2**. We obtained the following values:

$$\mathbf{1},\ \beta_{\text{spiro}}\ (\text{PPP}) = 0.38\ \text{eV}$$

$$\mathbf{2},\ \beta_{\text{spiro}}\ (\text{PPP}) = 0.32\ \text{eV}$$

To derive the resonance integrals from the MINDO/3 calculations first-order perturbation theory has been applied.[27] Accordingly the split $\Delta\epsilon$ between bands 3 and 4 in the PE spectra of **1** and **2** is given by (4).[5b] In this

$$\Delta\epsilon = 2(c_1c_1' - c_1c_w - c_wc_1' + c_wc_w')\beta_{\text{spiro}} \qquad (4)$$

equation c_1, c_1', c_w, and c_w' are defined as the AO coefficients at the heteroatoms in the wave functions. With the coefficients from the MINDO/3 calculation on **22** and **39** respectively, the following resonance integrals were obtained:

$$\mathbf{1},\ \beta_{\text{spiro}}\ (\text{MINDO/3}) = 0.48\ \text{eV}$$

$$\mathbf{2},\ \beta_{\text{spiro}}\ (\text{MINDO/3}) = 0.36\ \text{eV}$$

The resonance integrals obtained by this procedure are in fair agreement with the PPP results and with those obtained for **10**–**14**.[4] The similar values obtained for **1** and **2** are in line with the result that the overlap integrals between the nitrogen atoms in **1** are close to those between the sulfur atoms in **2**.

The sequences suggested by the calculations for bands 5–8 agree in the case of **1** and **22** with those presented in Figure 3. For **2** and **39**, however, the sequence differs. Due to the small separation of bands and energy levels an unambiguous explanation is not possible at present.

PE Spectra of 3 and 4. The PE spectra of **3** and **4** as well as of **31** and **40** are shown in Figure 4. The recorded ionization energies of all four compounds are listed in Table II. The PE spectrum of **31** shows two relatively broad bands between 8 and 11 eV while that of **40** exhibits four bands below 11 eV. The PE spectrum of **3** is very similar to those of **31**, the main difference being a broadening of the bands for the spirocompound **3**. In the PE

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[27] Heilbronner, E.; Bock, H. "Das HMO Modell und seine Anwendung"; Verlag Chemie: Weinheim, 1968. Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

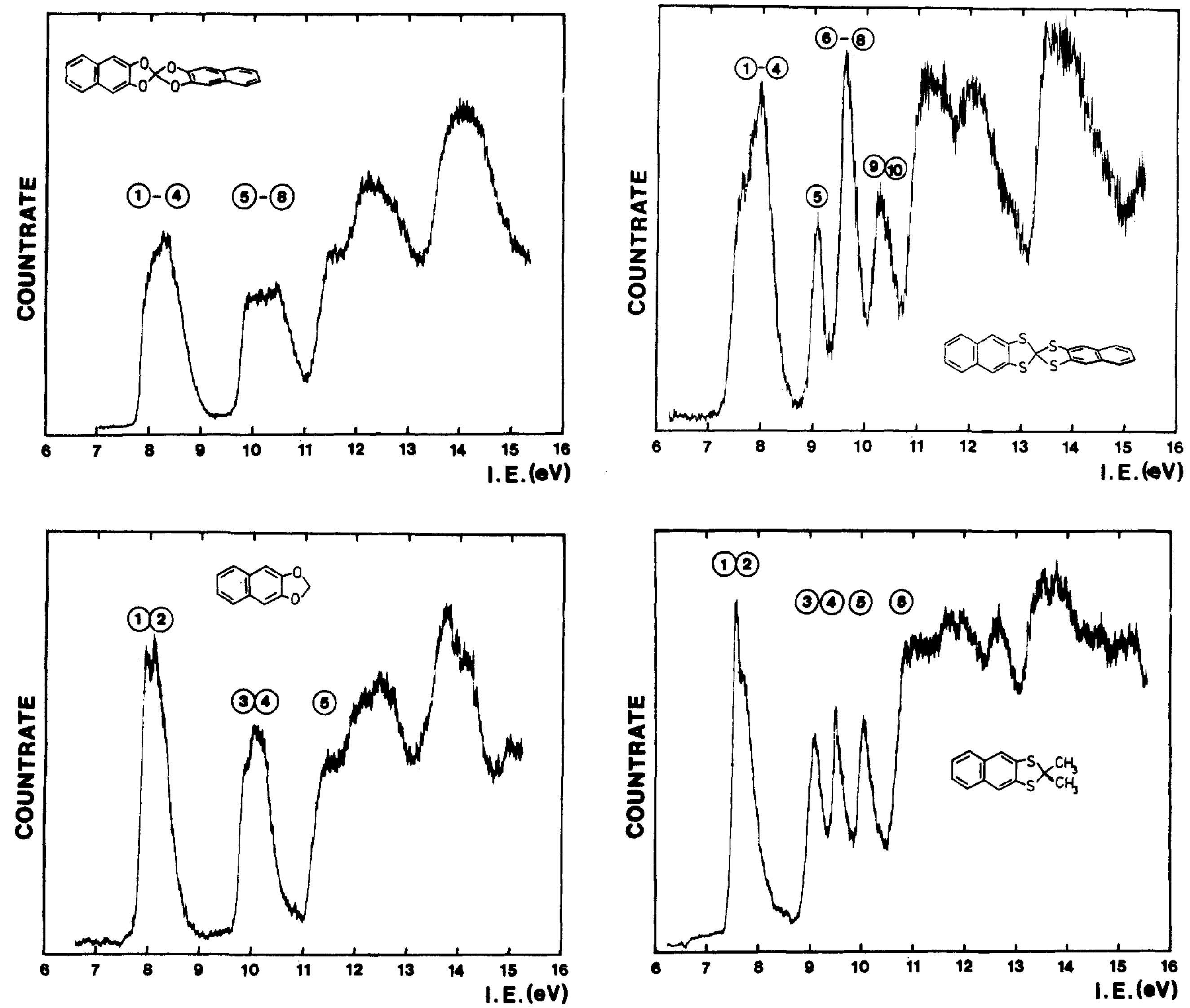

Figure 4. PE spectra of 3, 4, 31, and 40.

spectrum of 4 four bands below 11 eV can be clearly seen, and these are quite similar in energy to those found for 40.

As before it seems reasonable to assume that the bands below 11 eV result from ionization out of π-MO's. Also in the case of the sulfur species, the lone pairs on sulfur with 3s character are expected to occur at higher energies.[28] To assign the PE spectra of 3, 4, 31, and 40 empirically, we first consider the highest occupied π-MO's of a naphthalene unit substituted at positions 2 and 3 with two heteroatoms such as oxygen or sulfur respectively. On the left side of Figure 5 are presented the expected MO sequences as well as the π-MO's. One can recognize two energetically very similar MO's ($4b_1$, $3a_2$), separated considerably from three further π-MO's of the same symmetry ($2a_2$, $3b_1$, $1a_2$). Joining both fragments together would therefore yield four MO's at high orbital energies followed by six at low energies. The four MO's at high energy are predicted to be close together since the AO coefficients at the heteroatoms are small.

Thus even in the case of $3a_2$, in which spirointeraction is possible, the split is anticipated to be small. A similar, small interaction is predicted for $1a_2$ while for $2a_2$ a sizeable splitting in the corresponding spirocompound can be expected.

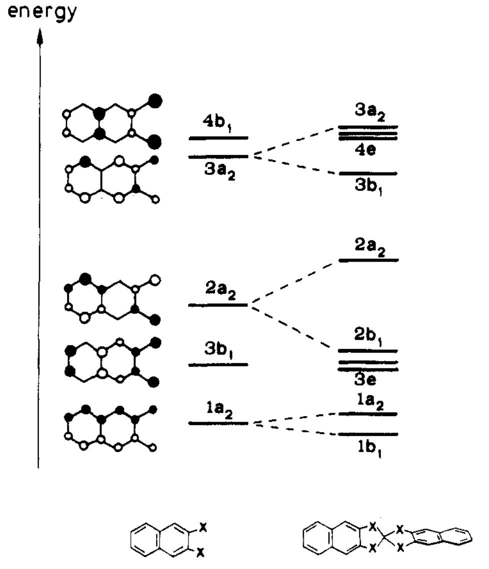

Figure 5. Schematic correlation between the highest occupied π-orbitals of a 2,3-diheterosubstituted naphthalene fragment with the corresponding spirocompound.

The diagram in Figure 5 agrees with the conclusions reached when comparing the spectra of 3 and 31 as well as of 4 and 40. In Figure 6 we have correlated the first bands of the PE spectrum of 40 with those of 4. If we

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(28) Gleiter, R.; Spanget-Larsen, J. *Top. Curr. Chem.* **1979**, *86*, 139.

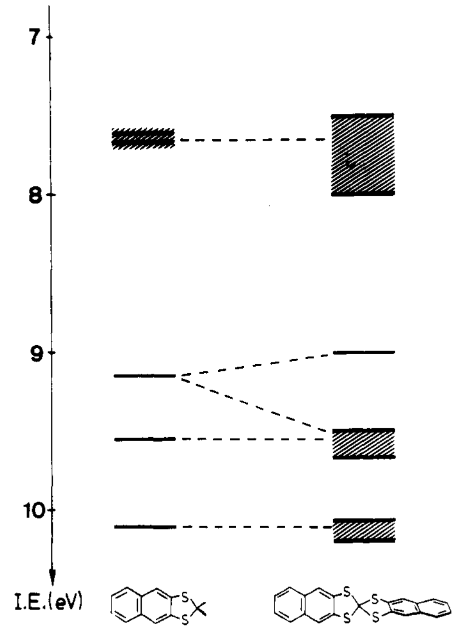

Figure 6. Comparison between the first bands of the PE spectra of **40** with those of **4**.

Table II. Measured Vertical Ionization Energies ($I_{v,j}$, eV) and Calculated Orbital Energies (ϵ_j) of 3, 4, 31, and 40

compd	band	$I_{v,j}$	assignment	$-\epsilon_j$ PPP	$-\epsilon_j$ MINDO/3
3	1	7.9–8.6	3 a_2[a]	7.76	8.23
	2		3 b_1	7.93	8.26
	3 4		4 e	8.23	8.28
	5	9.8–10.7	2 a_2	9.75	10.14
	6		2 b_1	9.92	10.20
	7 8		3 e	10.21	10.25
4	1	7.5–8.0	3 a_2[a]	7.50	7.99
	2 3		4 e	7.68	8.00
	4		3 b_1	7.76	8.27
	5	9.0	2 a_2	8.89	9.23
	6	9.5	2 b_1	9.54	10.03
	7 8		3 e	9.57	9.27
	9	10.15	1 a_2	10.17	10.56
	10		1 b_1	10.44	11.21
31	1	7.88	3 a_2[a]	7.55	8.18
	2	8.06	4 b_1	7.64	8.23
	3	10.0	2 a_2	9.54	10.14
	4		3 b_1	9.80	10.41
40	1	7.63	4 b_1[a]	7.52	8.16
	2		3 a_2	7.55	8.21
	3	9.15	2 a_2	9.10	9.66
	4	9.55	3 b_1	9.46	9.83
	5	10.10	1 a_2	10.10	10.72
	6	10.9	10 $b_2(\sigma)$		8.97

[a] The numbers refer to the π-systems only.

adopt for **40** the sequence indicated, the split between bands 5 and 6 in the PE spectrum of **4** should be caused by the spirointeractions.

The assignment given in Figure 6 is in line with the results of MO calculations considering the π-system only (PPP type). The calculated orbital energies for **3** and **4** are listed in Table II. The agreement between the observed spectra and the calculations is satisfactory.

PE Spectra of 5 and 6. The analysis of the PE spectra of **3** and **4** is hampered by the overlap of bands which are split due to spiroconjugation with other bands. Our MO calculations on **5** and **6** suggest for both compounds a sequence of MO's which is more readily treated than in the cases of **3** and **4**. To demonstrate this we have compared in Figure 7 the π-MO sequence of a 1,8-diheterosubstituted naphthalene unit with that of the corresponding spirocompound. It is seen that $2a_2$ and $3a_2$ (left side) are predicted to be well separated from those π-MO's which belong to the irreducible representation B_1.

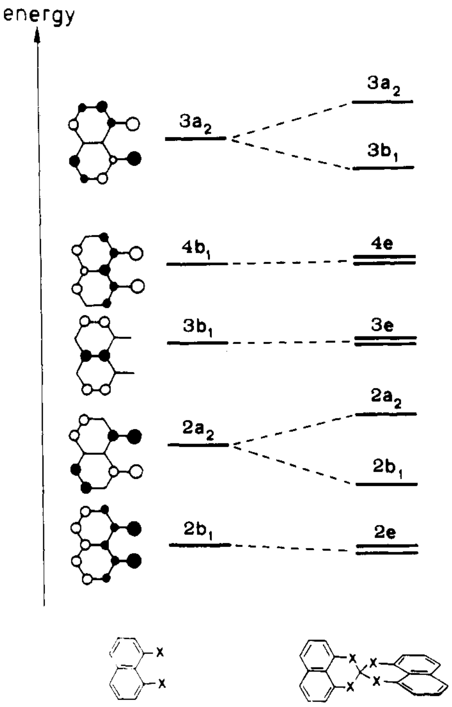

Figure 7. Schematic correlation between the highest occupied π-MO's of a 1,8-diheterosubstituted naphthalene moiety and the corresponding spirocompound.

Table III. Measured Vertical Ionization Energies ($I_{v,j}$, eV) of 23–25 and Calculated Orbital Energies (ϵ_j) of 23

band	**23**	**24**	**25**	assignment[a]	$-\epsilon_j$ (PPP)
1	6.90	6.88	6.85	3 a_2	6.79
2	7.8	8.0	8.0	4 b_1	7.92
3	8.5	8.43	8.4	3 b_1	8.78
4	9.4	8.92	8.8	2 a_2	9.69
5	10.08	9.91	9.9	2 b_1	10.72

[a] The numbers refer to the π-orbitals of **23**.

In **5** and **6**, the heteroatoms are part of a six-membered ring which is likely to be nonplanar.[11] To investigate the effect of conformational changes on the π-MO sequence[12,29] we have investigated the PE spectra of **23**–**25**. The PE spectrum of **23** is shown in Figure 8 as a representative example, while the recorded ionization energies of all three compounds are listed in Table III. A comparison between the three compounds yields nearly identical spectra for **24** and **25**. Between **23** and **24**, however, the energies of bands 2 and 4 differ considerably. In going from **23** to **24** band 2 is shifted toward higher energy, while band 4 is shifted towards lower energy.

We will use arguments derived from first-order perturbation theory[27] to show that these differences are due to conformational changes.

The planar system of the naphthalene ring imposes an envelope shape on the six-membered heterocyclic ring as shown. This shape implies a nearly eclipsed arrangement

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[29] Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14; **1981**, *14*, 131. Klessinger, M.; Rademacher, P. *Angew. Chem.* **1979**, *91*, 885; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 826.

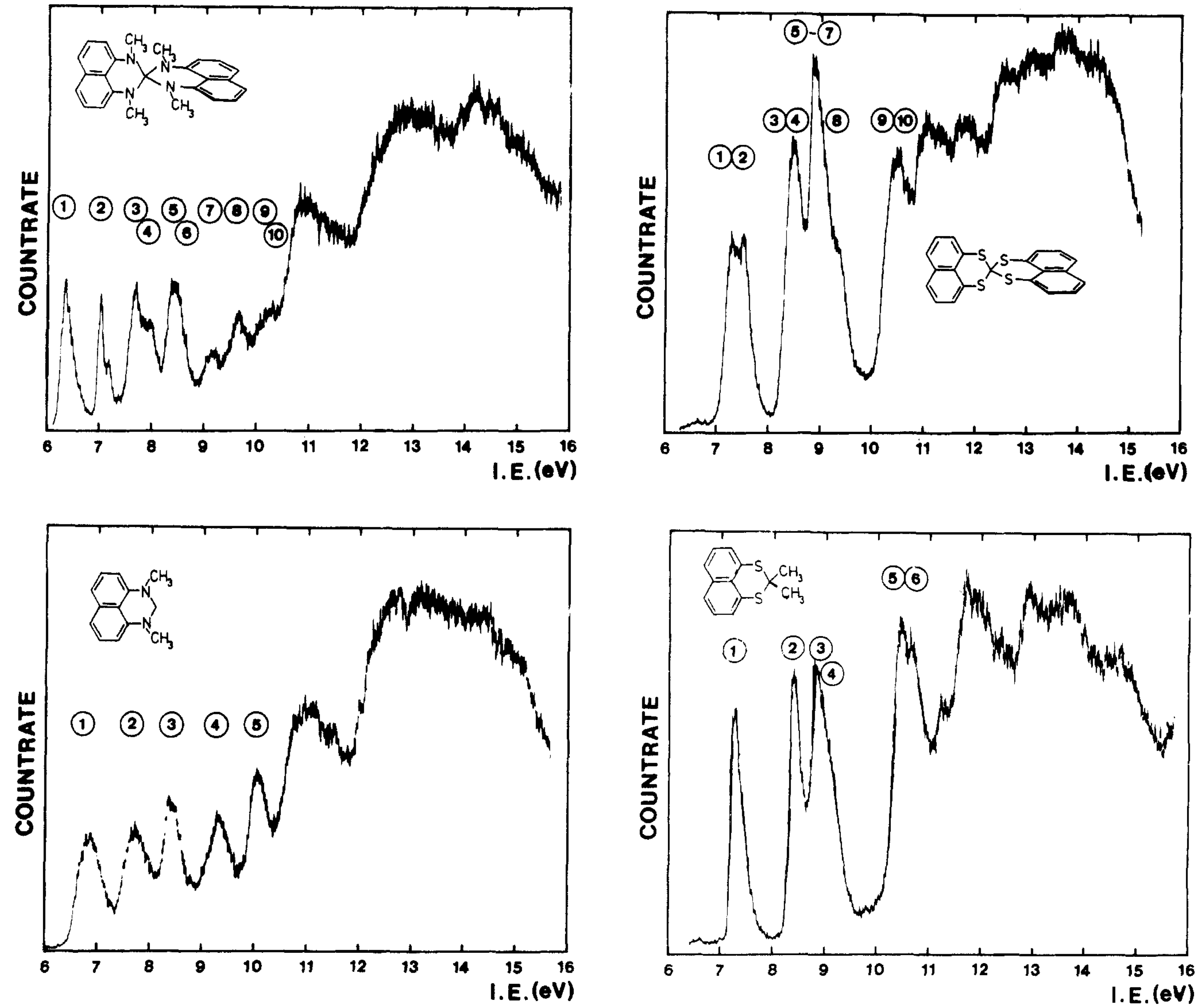
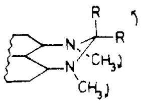


Figure 8. PE spectra of 5, 6, 23, and 41.

between the N–CH_3 σ-bond and the equatorial C–R σ-bond at the sp^3 center. Such a situation we assume in **23** (R = H). In **24** and **25**, however, where the substituents at the sp^3 center are bulkier than in **23** a bending of the *N*-methyl groups and the CR_2 fragment in opposite directions, as indicated by the arrows, should be reason to reduce steric strain. As a consequence the folding of the six-membered ring is increased.



To understand the consequences of nonplanarity on the orbital energies, we will consider the highest occupied MO's of the 1,8-diheterosubstituted naphthalene fragment (shown on the left of Figure 7). The bending of the sp^3 center in the sense indicated above will have two effects: it will reduce the overlap between the 2p atomic orbitals on the nitrogen atom and the π-system, but it will increase the interaction between the two nitrogen centers, since both substituents are bent out of the molecular plane.

Reduction of the overlap integral between a substituent and the ring will lower the energies of those MO's that have a node between centers 1 or 8 and the heteroatoms ($3a_2$, $4b_1$) and will raise those MO's that are bonding between centers 1 or 8 and the heterosubstituents ($2b_1$, $2a_2$). Increase of the nitrogen–nitrogen through-space interaction will raise $3a_2$ and $2a_2$ but lower $4b_1$ and $2b_1$. In our first-order treatment it can be assumed that both interactions should cancel each other for $3a_2$ and $2b_1$, while $4b_1$ should be lowered and $2a_2$ should be raised. The orbital $3b_1$ should be unaffected by geometrical changes because its wave function is localized at the naphthalene moiety. The expectations, described above are indeed found when the hydrogens at the sp^3 center of **23** are replaced by bulkier substituents such as in **24** or **25**. From these studies we conclude that in **24**, **25**, and **5** the six-membered ring deviates markedly from planarity. For **6** even a stronger deviation is anticipated, judging from investigations on 1,3-dithiane.[30]

After taking care of steric factors, we can discuss the PE spectra of **5** and **6** together with those of **23** and **41**. All four spectra are shown in Figure 8. A comparison between the spectra of **5** and **23** confirms our expectations. Bands 1 and 4 of **23** can be correlated with two bands in the spirocompound, while bands 2, 3, and 5 can only be correlated with one (broadened) band. The comparison between **6** and **41** looks less favorable, as both spectra are very similar, indicating only small splits due to spirointeraction.

In Table IV we have collected the ionization energies of **5**, **6**, and **41**. The splitting encountered for **5** amounts

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[30] Adams, W. J.; Bartell, L. S. *J. Mol. Struct.* **1977**, *37*, 261.

Table IV. Measured Vertical Ionization Energies ($I_{v,j}$, eV) and Calculated Orbital Energies (ϵ_j) of 5, 6, and 41

				$-\epsilon_j$	
compd	band	$I_{v,j}$	assignment	PPP	MINDO/3
5	1	6.35	3 a_2[b]	6.80	7.11[a]
	2	7.02	3 b_1	7.47	7.35
	3	7.63	15 e	8.42	8.35
	4	7.8			
	5 6	8.3	14 e	9.09	8.84
	7	9.1	2 a_2	9.69	10.14
	8	9.56	2 b_1	10.42	10.63
	9 10	10.2	13 e	11.09	10.74
6	1	7.3	3 a_2[b]	7.21	7.50
	2	7.5	3 b_1	7.42	7.99
	3 4	8.5	15 e	8.39	8.21
	5	8.9	14 e	8.97	8.96
	6				
	7		2 a_2	9.44	9.44
	8	9.3	2 b_1	9.82	10.75
	9 10	10.5	13 e	10.61	11.42
41	1	7.33	3 a_2[b]	7.17	7.83
	2	8.46	5 b_1	8.20	8.80
	3	8.86	4 b_1	8.86	9.00
	4	9.2	2 a_2	9.46	10.07
	5	10.5	3 b_1	10.48	10.92
	6	10.7	11 $b_2(\sigma)$		8.86

[a] In the calculations the methyl groups were replaced by H. [b] The numbers refer to the valence orbitals only.

Table V. Vertical Ionization Energies ($I_{v,j}$, eV) of 7–9

band	7	8	9
1	6.50	6.9	8.0
2	7.0	7.7	8.4
3	7.9		
4	8.1	8.4	9.3
5	8.4		10.0
6	9.4	9.5	10.4
7	10.5	10.1	11.5

to 0.67 eV for bands 1 and 2. Using the PPP method as described above, we obtain for the spiroresonance integral a value of 0.56 eV. If we assign $2a_2$ and $2b_1$ to bands 7 and 8 the observed split (0.47 eV) between these bands yields 0.34 eV for the spiroresonance integral. The splitting found between the first two bands of **6** is rather small, probably caused by stronger deviations from planarity as compared to other six-membered rings containing sulfur centers.[30]

In Table IV we also list the results of MO calculations considering the π-MO's only (PPP model).[23] The agreement between calculated orbital energies and measured ionization energies is satisfactory. Our assignment suggested for **41** agrees with that proposed for the parent compound.[31]

PE Spectra of 7–9. In compounds **7–9** both molecular fragments are different, and therefore all three belong at most to point group C_{2v}. From our previous studies on spirocompounds with differing fragments[4,5d] we anticipate in all three compounds little or no interaction between the fragments. Nevertheless we will report these PE spectra because we recorded these data in connection with our electrochemical and electron spectroscopic investigations of **7–9**.

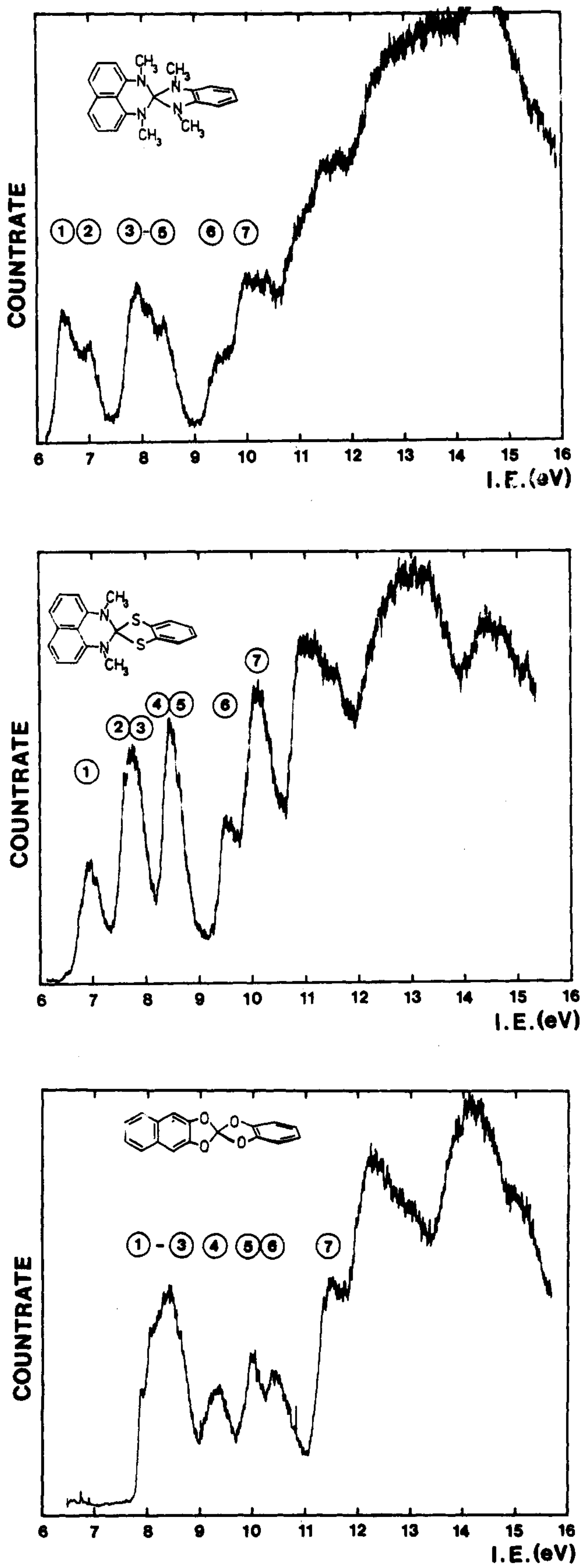

Figure 9. PE spectra of 7–9.

All three PE spectra are shown in Figure 9 and the corresponding vertical ionization energies are listed in Table V. The PE spectrum of **7** shows two close-lying bands at 6.5 and 7.0 eV followed by a peak consisting of three strongly overlapping bands, separated from a shoulder at 9.4 eV and a broad band at 10 eV. The PE

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(31) Bock, H.; Brähler, G.; Dauplaise, D.; Meinwald, J. *Chem. Ber.* 1981, *114*, 2622.

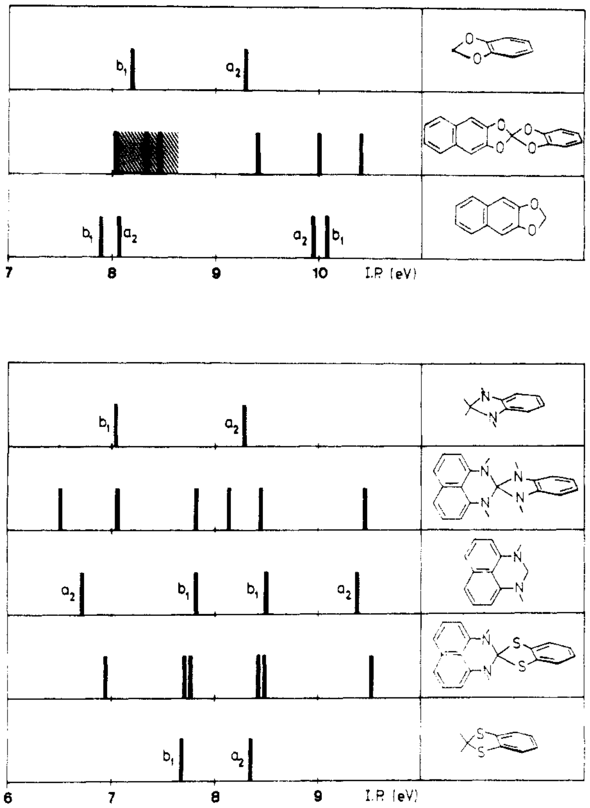

Figure 10. Comparison between the first bands in the PE spectra of **7**–**9** with those of the fragments **23**, **31**, **39**, and **44**–**45**.

spectrum of **8** displays five peaks below 10.5 eV in the approximate intensity ratio of 1:2:2:1:3. In the PE spectrum of **9** the approximate intensity ratio of the first four peaks amounts of 3:1:1:1.

A comparison of the PE spectra of **7**–**9** with those of the appropriate fragments is presented in Figure 10. In this Figure, the PE spectrum of **7** is compared with those of **23** and 2,3-dihydro-1,3-dimethyl-1*H*-benzimdiazole (**44**),[4] that of **8** with those of **23** and **39**, and that of **9** with those of **31** and 1,3-benzodioxole (**45**).[4]

In all three cases the spectra of the spirocompounds are very close to those of the superimposed PE spectra of the fragments, indicating at most only very weak interactions between the fragments.

Concluding Remarks. Our investigations on **1**–**6** have shown rather large spirointeractions for **1**, **2**, **4**, and **5**. In the case of **4** and especially of **3** the splitting of the bands is not easy to recognize because of their substantial overlap. The small spirointeractions found for **6** are probably due to a considerable deviation of the heterorings from planarity. The most interesting effects with respect to reactivity can be expected to occur for **5** and to a lesser degree for **6**, because in these compounds the highest occupied MO's are affected by spiroconjugation.

Experimental Section

General. Melting points were determined with a Büchi apparatus (model Dr. Tottoli) and are uncorrected. ^{1}H NMR spectra were measured on a Varian EM 390 (90 MHz), Varian EM 360 (60 MHz), and Bruker WH 300 (300 MHz) instruments with Me_4Si as internal standard. ^{13}C NMR spectra were obtained with a Varian CFT-20 (20 MHz) and Bruker WH 300 (75.46 MHz) instruments with Me_4Si as internal standard. High-resolution mass spectra were recorded on a ZAB instrument (Vacuum-Generators) at an ionizing energy of 70 eV. Chemical ionization mass spectra (CIMS) were recorded on a Finnigan 3200 GC/MS. The He I_α photoelectron spectra were recorded on a Perkin-Elmer PS 18 and UPG 200 spectrometers of Leybold Heraeus. The calibration has been carried out with Xe and Ar. A resolution of ±0.04 eV was achieved for the single bands and of ±0.1 eV for the shoulders. Elemental analysis were performed by the microanalytical laboratory of the University Heidelberg.

4,5,*N*,*N*′-Tetramethyl-*o*-phenylenediamine (15). 2,5,6-Trimethylbenzimidazole[32] (29 g, 0.18 mol) was dissolved in 300 mL of anhydrous acetontrile under nitrogen, and 38 g of anhydrous sodium carbonate (0.36 mol) was added. Under stirring and refluxing, 57 g of dimethyl sulfate was added within 1 h. After the mixture was refluxed for another hour, 50 mL of water was added and stirred at room temperature (for 10 min). The acetonitrile was removed under vacuum, and 500 mL of diluted HCl, was carefully added until pH 1. This was followed by addition of a concentrated solution of 45 g (0.27 mol) of KI in H_2O. After the mixture was stirred for 10 min the precipitate was removed by filtration and dried. After recrystallization from acetonitrile, 40 g (70%) of 1,2,3,5,6-pentamethylbenzimidazolium iodide was obtained: colorless crystals, mp 327 °C dec; ^{1}H NMR (CF_3CO_2D) δ 2.5 (s, 6 H), 2.92 (s, 3 H), 4.00 (s, 6 H), 7.50 (s, 2 H). The crystals were hydrolyzed by refluxing under N_2 with 40 g of KOH in 150 mL of glycol monomethyl ether for 15 h. After the addition of 150 mL of H_2O, the water phase was washed with ether. After the drying of the organic phase (KOH), the ether was removed. The residue was purified by vacuum distillation; 16.8 g (81%) of a yellow solid was obtained: bp 95–96 °C (0.15 mmHg); mp 52–55 °C; ^{1}H NMR ($CDCl_3$) δ 2.15 (br s, 6 H), 2.5–3.3 (m, 8 H), 6.4 (s, 2 H).

2-Chloro-1,3,5,6-tetramethylbenzimidazolium Tetrafluoroborate (16). This compound has been prepared in an analogous fashion to that reported in ref 8 from 1.74 g (9 mmol) of 2-chloro-1,5,6-trimethylbenzimidazole[33] and 1.32 g (9 mmol) of trimethyloxonium tetrafluoroborate; 2.3 g (87%) of colorless crystals were obtained: mp 254–256 °C; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 6 H), 3.95 (s, 6 H), 7.60 (s, 2 H).

1,1′,3,3′,5,5′,6,6′-Octamethyl-2,2′-spirobi[2,3-dihydro-1*H*-benzimidazole] (1). This compound was prepared in an analogous fashion to that reported in ref 8 by refluxing under N_2 a solution of 1.04 g (6.3 mmol) of **15**, 1.8 g (6.1 mmol) of **16**, and 2 g (20 mmol) of triethylamine in 20 mL of dry acetonitrile for 3 h. After the mixture was kept for 12 h at room temperature, colorless crystals were obtained. Recrystallization from acetonitrile yielded 1.5 g (73%) of **1**: mp 182–183 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 12 H), 2.60 (s, 12 H), 6.15 (s, 4 H). Anal. Calcd for $C_{21}H_{28}N_4$: C, 74.96; H, 8.39; N, 16.65. Found: C, 74.74; H, 8.63; N, 16.74.

2-Chloro-1-methyl-1*H*-perimidine (19). 2-Chloro-1*H*-perimidine (**18**)[9,10] (23.0 g, 114 mmol), 18.0 g (0.17 mol) of anhydrous Na_2CO_3, and 18.0 g (0.13 mol) of methyl iodide were stirred for 4 h in 200 mL of oxygen-free Me_2SO. $CHCl_3$ (200 mL) and 600 mL of H_2O were added; the mixture was stirred and filtered. The organic phase was washed two times with water and dried ($MgSO_4$). After evaporation an oily residue remained which solidified to 21.3 g (86%) of a yellow mass, mp 88 °C (lit[10] mp 98–99 °C). For further reactions a purification was not necessary.

2-Chloro-1,3-dimethylperimidinium Tetrafluoroborate (20). To a solution of 10 g (46 mmol) of **19** in 80 mL of dry 1,2-dichloroethane was added 6.3 g (43 mmol) of trimethyloxonium tetrafluoroborate. Shortly after the addition was finished a yellow solid started to precipitate. After being stirred of 15 h, the mixture was filtered and the precipitate washed with dry 1,2-dichloroethane. For purification the yellow solid was dissolved in a small portion of dry acetonitrile. After the addition of a fourfold amount of dry ether the precipitate was filtered off to give 7.6 g (49%) of a yellow powder: mp 225 °C dec; ^{1}H NMR (CD_3CN) δ 3.75 (s, 6 H), 7.07 (dd, J = 7.2 Hz, J = 1.5 Hz, 2 H, 4-, 9-H), 7.3–7.9 (m, 4 H). Anal. Calcd. for $C_{13}H_{12}ClN_2BF_4$: C, 49.02; H, 3.80; N, 8.80. Found: C, 49.29; H, 4.09; N, 8.58.

1,1′,3,3′-Tetramethyl-2,2′-spirobi[2,3-dihydro-1*H*-perimidine] (5). To a solution of 5.0 g (27 mmol) of *N*,*N*′-dimethyl-1,8-diaminonaphthalene (**21**)[11] and 7.0 g (69 mmol) of triethylamine in 100 mL of dry, oxygen-free acetonitrile was added 8 g (25 mmol) of **20** with stirring. After the mixture was stirred for

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3 h, 3.6 g of **5** (38%) precipitated; mp 350 °C. The nearly colorless powder can be purified by recrystallization from chlorobenzene under nitrogen: ^{1}H NMR ($CDCl_3$) δ 2.77 (s, 12 H), 6.33 (dd, J = 7.5 Hz, J = 1 Hz, 4 H, 4-, 4′-, 9-, 9′-H), 7.02–7.40 (m, 8 H). Anal. Calcd for $C_{25}H_{24}N_4$: C, 78.92; H, 6.38; N, 14.73. Found: C, 78.92; H, 6.63; N, 14.74.

2,3-Dihydro-1,3-dimethyl-1*H*-perimidine (23). A solution of 2 g (10.8 mmol) of **21**[11] and 3 g of a 40% solution of formaldehyde (40 mmol) in 50 mL of dioxane was stirred for 3 h under a N_2 atmosphere. Afterwards 50 mL of methylene chloride and 200 mL of H_2O were added. The methylene chloride phase was separated, washed with water, dried ($MgSO_4$), and evaporated. The residue was sublimed at 0.2 mmHg and a bath temperature of 120 °C. This yielded 1.7 g (80%) of colorless crystals: mp 147–148 °C (lit.[13] mp 150 °C); ^{1}H NMR ($CDCl_3$) δ 2.93 (s, 6 H), 4.05 (s, 2 H), 6.45 (dd, J = 6.9 Hz, J = 1.7 Hz, 2 H, 4-, 9-H), 7.08–7.40 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 144.4 (C-3a), 134.8 (C-6a), 126.8 (C-5), 117.6 (C-6), 115.0 (C-9b), 103.4 (C-4), 70.5 (NCH_2N), 36.9 (NCH_3).

General Procedure for the Preparation of the 2,3-Dihydroperimidines 24 and 25. A solution of 8 mmol of *N,N′*-dimethylnaphthalene-1,8-diamine (**21**),[11] 24 mmol of the ketone, and 0.4 g of *p*-toluenesulfonic acid in 25 mL of benzene was stirred under N_2 at room temperature for 15 h. After washing with an aqueous solution of $NaHCO_3$, drying (Na_2SO_4), and removing of the solvents, we obtained an oily residue.

2,3-Dihydro-1,2,2,3-tetramethyl-1*H*-perimidine (24).[14] The oil was sublimed at 0.1 torr and 90–110 °C bath temperature to give 1.5 g (82%) of colorless crystals: mp 62 °C; ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 6 H), 2.9 (s, 6 H), 6.55 (dd, J = 6.7, 1.7 Hz, 2 H, 4-, 9-H) 7.1–7.4 (m, 4 H).

1′,3′-Dimethylspiro[cyclopentane-2,2′-[2,3]dihydro[1*H*]-perimidine] (25). The oil was distilled: bp 80 °C (0.1 torr); $n^{20}{}_D$ 1.6542; ^{1}H NMR ($CDCl_3$) δ 1.6–1.9 (m, 8 H), 2.8 (s, 6 H), 6.7 (dd, 2 H, 4-, 9-H), 7.1–7.4 (m, 4 H).

Naphtho[2,3-*d*]-1,3-dioxole-2-thione (26).[34] To a stirred suspension of 10 g (63 mmol) of naphthalene-2,3-diol (**27**) and 17 g (160 mmol) of anhydrous Na_2CO_3 in 120 mL of water was added 6 mL (78 mmol) of thiophosgene dropwise under nitrogen (water cooling). The red precipitate was filtered and washed with methanol. Purification was achieved by sublimation at 0.1 torr and 250 °C bath temperature: 11.5 g (91%) of pale yellow crystals, mp 284 °C; ^{1}H NMR (Me_2SO-d_6) δ 7.55–8.13 (AA′BB′, 4 H), 8.13 (s, 2 H, 4-, 9-H).

2,2′-Spirobi[naphtho[2,3-*d*]-1,3-dioxole] (3). A mixture of 1.5 g (7.4 mmol) of **26**, 2.3 g (7.2 mmol) of mercury diacetate, and 1.2 g (7.4 mmol) of naphthalene-2,3-diol (**27**) in 40 mL of dry THF was stirred under reflux for 5 h. After 1 h, a further 1.1 g (3.5 mmol) of mercury diacetate and 0.7 g (4.4 mmol) of **27** were added and refluxed for 4 h. After removal of the solvent, the residue was treated with 60 mL of $CHCl_3$, filtered, and chromatographed over basic Al_2O_3. The first fraction yielded **3**, which was recrystallized from toluene: 0.51 g (21%) of colorless crystals, mp 265.5–266.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.38 (s, 4 H, 4-, 4′-, 9-, 9′-H), 7.38–7.85 (AA′BB′, 8 H); (IMS, *m/e* 328 (M^+). Anal. Calcd for $C_{21}H_{12}O_4$: C, 76.82; H, 3.68. Found: C, 76.66; H, 3.67.

2,3-Dibromonaphthalene (36). This compound was prepared according to the procedure of Danish et al.[35] The pyrolysis of the Diels–Alder adduct from **36** and hexachlorocyclopentadiene was carried out at 220 °C (15 torr). Under these conditions nearly pure **36** distilled over together with hexachlorocyclopentadiene. The latter was removed by filtration and washing with ethanol.

2,3-Bis(benzylthio)naphthalene (38). A mixture of 24 g (84 mmol) of 2,3-dibromonaphthalene (**36**),[35] 22 mL (188 mmol) of benzylmercaptan, and 16 g (120 mmol) of powdered Cu_2O in 250 mL of pyridine was refluxed with stirring for 1 week. At the beginning the sludge was hard to stir but after 2 h it changed. The pyridine was evaporated at 100 mmHg. To remove residual pyridine, 100 mL of toluene was added with subsequent evaporation at reduced pressure. The residue was shortly refluxed with 200 mL of toluene. After hot filtration and removal of the solvent the residue was chromatographed on silica gel with toluene. The first fraction was recrystallized from ethyl acetate: 22 g (70%) of colorless powder, mp 151–152 °C; ^{1}H NMR ($CDCl_3$) δ 4.17 (s, 4 H, SCH), 7.2–7.7 (m, 16 H).

Naphthalene-2,3-dithiol (35). **38** (6.5 g, 17.5 mmol) was added to 100 mL of liquid ammonia and purged with N_2. At –60 °C, 1.6 g (70 mmol) of sodium was added in small pieces during 1 h. After the mixture was stirred for 1 h, 6 g of ammonium chloride was slowly added. The mixture was allowed to evaporate, and the residue was dissolved in a solution of 15 g of NaOH in 50 mL of oxygen-free water under N_2 and stirred. After filtration the solution was quickly acidified by dilute hydrochloric acid with cooling and stirring. The precipitate was filtered, dried, and recrystallized from toluene under N_2 to give 2.0 g (60%) of pure **35** as a colorless powder: mp 162–163 °C; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 2 H, SH), 7.15–7.65 (AA′BB′, 4 H), 7.6 (s, 2 H, 1-, 4-H).

2,2′-Spirobi[1,3-benzodithiole] (2). A mixture of 7.0 g (21 mmol) of benzene-1,2-dithiol (**33**),[19] 2.1 g (10.5 mmol) of tetramethyl orthothiocarbonate (**32**),[36] and 100 mg of *p*-toluenesulfonic acid in 50 mL of dry toluene was stirred under N_2 at reflux temperature for 15 h. After cooling, the solution was washed with a dilute solution of NaOH in water and dried. The toluene was evaporated and the residue dissolved in 50 mL of cyclohexane, stirred with charcoal, and filtered. After evaporation of the solvent the residue was recrystallized from methanol to yield 1.8 g (60%) of colorless crystals: mp 120 °C (lit.[37] mp 120–121 °C); ^{1}H NMR (CCl_4) δ 6.93–7.13 (m); ^{13}C NMR (CCl_4) δ 137.8 (s, C-3a), 126.9 (d, C-5), 122.4 (d, C-4).

2,2′-Spirobi[naphtho[1,8-*de*]-1,3-dithiin] (6). A mixture of 3.0 g (15.6 mmol) of naphthalene-1,8-dithiol,[20] 1.5 g (7.5 mmol) of tetramethyl orthothiocarbonate (**32**),[36] and 100 mg of *p*-toluenesulfonic acid in 50 mL of dry toluene was stirred and refluxed under N_2 for 30 h. After cooling, solid **6** was filtered, washed with ethanol, and recrystallized from toluene (charcoal); this yielded 1.2 g (41%) of a colorless powder: mp 268–269 °C; ^{1}H NMR ($CDCl_3$) δ 7.15–7.83 (m); CIMS, *m/e* 392 (M^+). Anal. Calcd for $C_{21}H_{12}S_4$: C, 64.25; H, 3.08; S, 32.67. Found: C, 64.46; H, 3.10; S, 32.56.

2,2′-Spirobi[naphtho[2,3-*d*]-1,3-dithiole] (4). This compound was prepared in an analogous fashion to that described for **6** by refluxing 3.0 g (15.6 mmol) of naphthalene-2,3-dithiol (**35**), 1.56 g (7.8 mmol) of tetramethyl orthothiocarbonate (**32**),[36] and 100 mg of *p*-toluenesulfonic acid in 60 mL of dry toluene under N_2 for 15 h. It yielded 1.6 g (52%) of colorless needles: mp 328 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.71 (s, 4 H, 4-, 4′-, 9-, 9′-H), 7.44–7.74 (AA′BB′, 8 H); CIMS, *m/e* 392 (M^+). Anal. Calcd for $C_{21}H_{12}S_4$: C, 64.25; H, 3.08; S, 32.67. Found: C, 64.09, H, 3.15; S, 32.82.

2,2-Dimethyl-1,3-benzodithiole (39).[38] A solution of 2 g (14.1 mmol) of benzene-1,2-dithiol (**33**),[19] 5 g of acetone, and 100 mg of *p*-toluenesulfonic acid in 20 mL of dry benzene was refluxed under N_2 for 15 h. After cooling, the organic layer was washed with a dilute solution of sodium carbonate in water and dried. After evaporation of the solvent the residue was dissolved in 40 mL of pentane and stirred with charcoal. Filtration and evaporation yielded 2.0 g (78%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 6 H), 6.8–7.2 (AA′BB′, 4 H). Anal. Calcd for $C_9H_{10}S_2$: C, 59.29; H, 5.53; S, 35.18. Found: C, 59.32; H, 5.75; S, 35.08.

2,2-Dimethylnaphtho[1,8-*de*]-1,3-dithiin (41). This compound was prepared in an analogous fashion as described for **39**, starting from 840 mg (4.4 mmol) of naphthalene-1,8-dithiol, 5 g of acetone, and 50 mg of *p*-toluenesulfonic acid. Purification was achieved by chromatography on silica gel with pentane as eluent. The obtained yellow oil solidified after standing, yielding 200 mg (69%) of a pale yellow solid: mp 61–62 °C; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 6 H), 7.13–7.66 (m, 6 H); CIMS, *m/e* 232 (M^+). Anal. Calcd for $C_{13}H_{12}S_2$: C, 67.19; H, 5.21; S, 27.60. Found: C, 67.11; H, 5.15; S, 27.50.

2,2-Dimethylnaphtho[2,3-*d*]-1,3-dithiole (40). A solution of 350 mg (1.82 mmol) of naphthalene-2,3-dithiol (**35**), 200 mg

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(3.45 mmol) of acetone, and 1 mL of $POCl_3$ in 20 mL of benzene was allowed to stand at room temperature under N_2 for 15 h. The solution was poured into ice-water and neutralized with $NaHCO_3$. The organic layer was separated, washed with water, dried, and evaporated to yield 380 mg (90%) of a colorless solid: mp 115.5–116.5 °C; ^1H NMR ($CDCl_3$) δ 1.92 (s, 6 H), 7.20–7.65 (AA′BB′, 4 H), 7.60 (s, 2 H, 4-, 9-H); CIMS, m/e 232 (M^+). Anal. Calcd for $C_{13}H_{12}S_2$: C, 67.18; H, 5.21; S, 27.60. Found: C, 67.34; H, 5.25; S, 27.58.

Spiro[1,3-benzodioxole-2,2′-naphtho[2,3-*d*][1,3]dioxole] (9). To a quickly stirred suspension of 8.0 g (50 mmol) of naphthalene-2,3-diol in 100 mL of dry CH_2Cl_2 was added dropwise over a period of 30 min a solution of 9.5 g (50 mmol) of 2,2-dichloro-1,3-benzodioxole[16] in 50 mL of dry CH_2Cl_2. During the addition the mixture was cooled by a water bath. After being stirred an additional hour, the mixture was filtered, the filtrate washed two times with water and dried, and the solvent removed. The dark residue was stirred with 100 mL of MeOH and filtered. The dark solid was dissolved in CCl_4 and chromatographed on silica gel. The first fractions were collected and recrystallized twice from isopropyl alcohol to yield 2.6 g (19%) of a colorless solid: mp 156–157 °C; ^1H NMR (CCl_4) δ 6.95 (m, 4 H), 7.24 (s, 2 H, 4′-, 9′-H), 7.25–7.75 (AA′BB′, 4 H). Anal. Calcd for $C_{17}H_{10}O_4$: C, 73.38; H, 3.62. Found: C, 73.18; H, 3.82.

1,1′,3,3′-Tetramethylspiro[2,3-dihydrobenzimidazole-2,2′-[2,3]dihydro[1*H*]perimidine] (7). 7 was prepared analogously to 1 from 1.5 g (15.60 mmol) of 2-chloro-1,3-dimethylbenzimidazolium tetrafluoroborate,[8] 1.04 g (5.60 mmol) of *N*,*N*′-dimethylnaphthalene-1,8-diamine (21),[11] and 1.2 g (12 mmol) of triethylamine in 25 mL of acetonitrile: yield, 1.35 g (73%) of a colorless solid, mp 325 °C dec; ^1H NMR ($CDCl_3$) δ 2.62 (s, 6 H), 2.68 (s, 6 H), 6.24–6.68 (AA′BB′, 4 H), 6.27–6.37 (dd, 2 H, 4′-, 9′-H), 7.03–7.38 (m, 4 H, 5′-, 6′-, 7′-, 8′-H); mass spectrum EIMS, (M^+) calcd 330.1844, obsd 330.1866. Anal. Calcd for $C_{21}H_{22}N_4$: C, 76.33; H, 6.71; N, 16.96. Found: C, 76.48; H, 6.81; N, 16.92.

1′,3′-Dimethylspiro[1,3-benzodithiole-2,2′-[2,3]dihydro-[1*H*]perimidine] (8). 8 was analogously prepared to 1 from 1.00 g (3.14 mmol) of 2-chloro-1,3-dimethylperimidinium tetrafluoroborate (20), 0.446 g (3.14 mmol) of benzene-1,2-dithiol,[19] and 0.7 g (6.9 mmol) of triethylamine in 40 mL of acetonitrile. The crude product was recrystallized from petroleum ether and charcoal to yield 350 mg (33%) of colorless needles: mp 187–188 °C; ^1H NMR ($CDCl_3$) δ 3.25 (s, 6 H), 6.25 (dd, J = 6.9, 2.3 Hz, 2 H, 4′-, 9′-H), 6.88–7.3 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 138.8 (C-3a′), 135.7 (C-3a), 133.7 (C-6a), 127.3 (C-5′ or C-5), 124.7 (C-5 or C-5′), 121.2 (C-4), 118.5 (C-6′), 113.2 (C-9b′), 104.5 (C-4′), 37.6 (NCH_3); EIMS, (M^+) calcd 336.0755, obsd 336.0746. Anal. Calcd for $C_{19}H_{16}N_2S_2$: C, 67.82; H, 4.79; N, 8.33; S, 19.06. Found: C, 67.79; H, 4.94; N, 8.09; S, 19.07.

Calculations. The PPP calculations were carried out with the parameters suggested by Zahradnik et al.[26] The core energy, I_C, for the lone pairs of the methylamino groups in **1**, **5**, and **23–25** was set equal to −26.3 eV. For **22** we reduced the value to −25.3 eV to take care of the inductive effect of the cyclopentane ring. In **1** and **22**, I_c for the carbon atoms bearing methyl groups was reduced by 1 eV (I_c = −10.40 eV) in order to account for the inductive effect of methyl groups in aromatic systems.[39]

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Registry No. 1, 99643-38-6; 2, 837-01-4; 3, 99643-39-7; 4, 99643-40-0; 5, 99643-41-1; 6, 99643-42-2; 7, 99643-43-3; 8, 99643-44-4; 9, 82823-46-9; 15, 75751-21-2; 16, 99643-47-7; 18, 30837-50-4; 19, 30837-60-6; 20, 99643-49-9; 21, 20734-56-9; 23, 37471-00-4; 24, 64482-94-6; 25, 99643-50-2; 26, 67177-41-7; 27, 92-44-4; 32, 6156-25-8; 33, 17534-15-5; 35, 99643-52-4; 36, 13214-70-5; 38, 99643-51-3; 39, 87473-92-5; 40, 99643-54-6; 41, 99643-53-5; 2,5,6-trimethylbenzimidazole, 3363-56-2; 1,2,3,5,6-pentamethylbenzimidazolium iodide, 99643-45-5; 2-chloro-1,5,6-trimethylbenzimidazole, 39791-97-4; trimethyloxonium tetrafluoroborate, 420-37-1; formaldehyde, 50-00-0; acetone, 67-64-1; cyclopentanone, 120-92-3; thiophosgene, 463-71-8; benzyl mercaptan, 100-53-8; naphthalene-1,8-dithiol, 25079-77-0; 2,2-dichloro-1,3-benzodioxole, 2032-75-9; 2-chloro-1,3-dimethylbenzimidazolium tetrafluoroborate, 18116-10-4.

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Synthesis of (−)-Methyl Ravidosaminide

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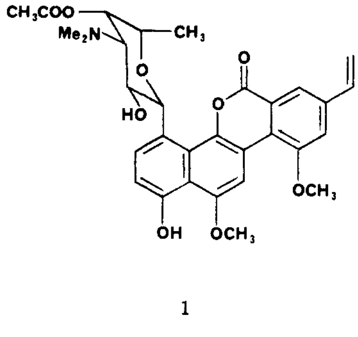
The title compound (**9b**) was prepared in five steps (48% overall yield) from ethyl 2,3,6-trideoxy-α-D-*erythro*-hex-2-enopyranoside (**4b**) as a 1:2.3 mixture of α- and β-anomers. The key step was the iodocyclization reaction of unsaturated carbonimidothioate derivative **5**. An improved procedure for the synthesis of **4b** is also described.

Ravidomycin (1), isolated[1,2] at Ayerst Laboratories by culturing a streptomycete found in a Guatemala soil sample, is an aromatic C-glycoside with antitumor and antibiotic properties.[1,3] It may be considered a derivative of the aminosugar 3,6-dideoxy-3-(*N*,*N*-dimethylamino)altropyranose (**9a**), herein referred to as ravidosamine[1] (the absolute configuration of this portion of **1** has not been determined). We became interested in the synthesis of **1** because of the cis, vicinal *N*,*N*-dimethylamino alcohol grouping at C-3,4 of **9a**. Based on our earlier work on aminocyclitol synthesis,[4,5] we believed this functionality



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