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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 26. 6,7-Dihydroacenaphtho[5,6-*cd*][1,2,6]thiadiazine and Acenaphtho[5,6-*cd*][1,2,6]thiadiazine

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Magnetic circular dichroism of acenaphtho[5,6-*cd*][1,2,6]thiadiazine and its 6,7-dihydro analogue is reported and interpreted. Polarization directions were obtained from linear dichroism in the UV–visible and IR regions measured in stretched polyethylene. It is concluded that the similarity of the absorption spectra of the two compounds is only superficial. Two transitions are characterized in the visible absorption band in acenaphtho[5,6-*cd*][1,2,6]thiadiazine, but only one is responsible for the apparently analogous band in the dihydro analogue. The spectroscopic properties of these compounds calculated by using the PPP-SCF approach agree well with the experimental spectra. The applicability of the perimeter model to the interpretation of their MCD signs is discussed.

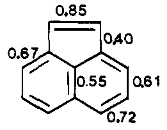
Putative hypervalent sulfur–nitrogen heterocycles are of current theoretical and experimental concern.[2] Our interest in the spectroscopy of acenaphthylene (1) and related molecules[3] led us to consider the spectroscopic behavior of acenaphtho[5,6-*cd*][1,2,6]thiadiazine (2) and its partially saturated analogue 6,7-dihydroacenaphtho-[5,6-*cd*][1,2,6]thiadiazine (3, Chart I). The sulfur diimide bridge in these thiadiazines constitutes an unusual perturbation of the all-carbon parent analogue with a charged perimeter and therefore offers an interesting test for the perimeter model which has been used successfully to characterize the magnetic circular dichroism (MCD) of π-electron systems derived from (4*N* + 2)-electron conjugated perimeters.[4]

In addition to measuring the MCD spectra of 2 and 3, we have determined the polarization directions of their electronic transitions from linear dichroism (LD) in the UV–visible and IR regions as measured in stretched polymer sheets. We analyze the results in terms of the simple perimeter model and in terms of the Pariser–Parr–Pople (PPP) π-electron theory.[5]

Bartetzko and Gleiter[2e] recently reported spectroscopic assignments for 3 using PPP calculations, LD, and photoelectron spectroscopic measurements. A comparison between their results and our MCD data makes possible a further assessment of the value of MCD spectroscopy in assigning spectroscopic transitions in complex molecules.

Experimental Section and Calculations

Chart I



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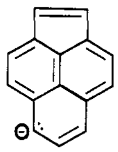

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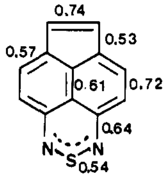

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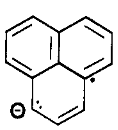

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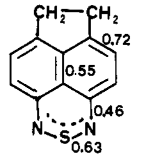

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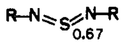

6

The samples were prepared by published methods[6] and purified by crystallization and vacuum sublimation. The 3-methylpentane (3MP) solvent (Phillips) was purified by shaking with sulfuric acid, washing, drying over sodium sulfate, and then distilling from sodium. 2-Methyltetrahydrofuran (MTHF) was distilled, stored over sodium benzophenone ketyl, and distilled on a vacuum line prior to use. MCD[7a] and LD (UV–visible[7b], IR[7c]) measurements were performed and analyzed as previously described (stepwise reduction for LD). The polarized IR spectra of 2 contain peaks due to transitions polarized along (i) the long axis (z), with $K_z = \langle \cos^2 z \rangle = 0.49$, located at 522 and 780 cm^{-1}, (ii) the short in-plane axis (y), with $K_y = \langle \cos^2 y \rangle = 0.36$, located at 496 and 945 cm^{-1}, and (iii) the out-of-plane axis (x), with $K_x = \langle \cos^2 x \rangle = 0.13$, located at 461 and 834 cm^{-1}. The spectra of 3 were much weaker and the resulting orientation factors less certain [$K_z = 0.50$ (639 cm^{-1}), $K_x = 0.14$ (833 cm^{-1})], while K_y could only be obtained by taking the difference to unity ($K_y = 0.36$). The fact that the differences between the orientation factors for the two

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(1) (a) Trinity University. (b) University of Utah.

(2) (a) Haddon, R. C.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1235. (b) Kaplan, M. L.; Haddon, R. C.; Schilling, F. C.; Marshall, J. H.; Bramwell, F. B. *Ibid.* **1979**, *101*, 3306. (c) Geiren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *Ibid.* **1979**, *101*, 7277. (d) Geiren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *Ibid.* **1980**, *102*, 5070. (e) Bartetzko, R.; Gleiter, R. *Angew, Chem., Int. Ed. Engl.* **1978**, *17*, 468. (f) Haddon, R. C.; Wasserman, S. R.; Wudl, F.; Williams, G. R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6687 and references therein. (g) Kaplan, M. L.; Haddon, R. C.; Hirani, A. M.; Schilling, F. C.; Marshall, J. H. *J. Org. Chem.* **1981**, *46*, 675.

(3) (a) Plummer, B. F.; Hopkinson, M. J. H.; Zoeller, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 6779. (b) Kenney, J. W.; Herold, D. A.; Michl, J.; Michl, J. *Ibid.* **1978**, *100*, 6884. (c) Thulstrup, E. W.; Michl, J. *Ibid.* **1976**, *98*, 4533. Kolc, J.; Michl, J. *Ibid.* **1976**, *98*, 4540; Michl, J. *Ibid.* **1976**, *98*, 4546. Michl, J.; Muller, J. F. *Ibid.* **1976**, *98*, 4550. (d) Wallace, S. L.; Michl. J. *Isr. J. Chem.* **1980**, *20*, 253.

(4) (a) Michl, J. *Pure Appl. Chem.* **1980**, *52*, 1549. (b) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801, 6812, 6819.

(5) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466, 767. Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.

(6) (a) Behringer, H.; Leiritz, K. *Chem. Ber.* **1965**, *98*, 3196. (b) Beecken, H. *Ibid.* **1967**, *100*, 2164. (c) Flowerday, P.; Perkins, M. J.; Arthur, A. R. J. *J. Chem. Soc. C* **1970**, 290.

(7) (a) Dewey, H. J.; Deger, H.; Frölich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412. (b) Thulstrup, E. W.; Downing, J. W.; Michl, J. *Chem. Phys.* **1977**, *23*, 307. Thulstrup, E. W.; Michl, J. *J. Phys. Chem.* **1980**, *84*, 82. (c) Radziszewski, J. G.; Michl, J. *Ibid.*, in press.

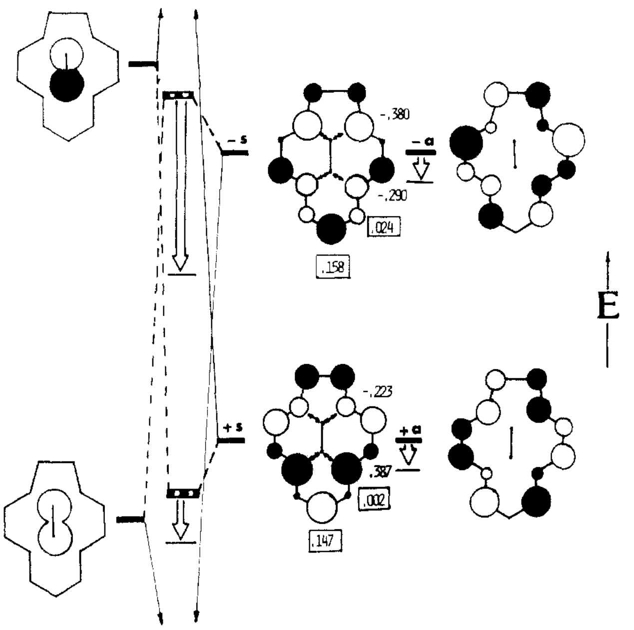

Figure 1. Effect of cross-linking and aza and thio substitution upon the molecular orbitals of the [13]annulenide anion. Numbers in boxes are squares of AO coefficients.

compounds lie within the experimental error is not surprising, considering their nearly identical shape. The knowledge of the orientation factors was used in the determination of purely polarized UV-visible spectra $A_z(\tilde{\nu})$ and $A_y(\tilde{\nu})$ from the measured parallel (E_z) and perpendicular ($E_\perp$) polarized experimental spectra, assuming negligible out-of-plane polarized absorption (eq 1 and 2).

$$A_z(\tilde{\nu}) = [(1 - K_y)E_Z(\tilde{\nu}) - 2K_yE_Y(\tilde{\nu})]/(K_z - K_y) \qquad (1)$$

$$A_y(\tilde{\nu}) = [2K_zE_Y(\tilde{\nu}) - (1 - K_z)E_Z(\tilde{\nu})]/(K_z - K_y) \qquad (2)$$

The calculations are of the standard PPP type, with literature parameters[8] being used for the values of the ionization potentials and electron affinities ($I_C = 11.42$, $I_N = 14.1$, $A_C = 0.58$, $A_N = 1.80$, $\beta_{CC} = \beta_{CN} = -2.318$, and $\beta_{NS} = -2.2$, all in electron volts). The calculated energies for the electronic transitions were relatively insensitive to parameter choices for sulfur and were in good agreement with the experimental results. In the case of **2**, the signs of the MCD B terms were rather sensitive to the choice of the sulfur parameters. Of the two choices given in ref 8, the choice of 20.27 eV for I_{S+} and 10.42 eV for A_{S+} produced results consistent with the experimental data. The calculations of B terms were performed as in ref 8 except that next-nearest-neighbor interactions were included in the calculation of the matrix elements of the magnetic moment operator by taking $\beta_{13} = -0.15\beta_{12}$ as recommended in ref 9.

Results and Discussion

Figures 1–4 and Table I show the experimental and calculated results. The assignment of eight electronic transitions in **2** and eight in **3** is proposed. Some transitions are clearly defined but a few of the assignments are only tentative. The first two transitions in **2**, 1 and 2, which overlap completely in absorption near 17 000 cm^{-1}, are verified as independent transitions differing in polarization and MCD signs. The assignment of four independent transitions within the strong absorption peak near 30 000 cm^{-1} is based on the MCD curve and must be considered tentative. The assignments for **3** are identical with those of ref 2e, except that the shape of the MCD curve suggests the presence of the two overlapping transitions 5 and 6 near 38 000 cm^{-1} and of the two overlapping transitions 7 and 8 near 45 000 cm^{-1}.

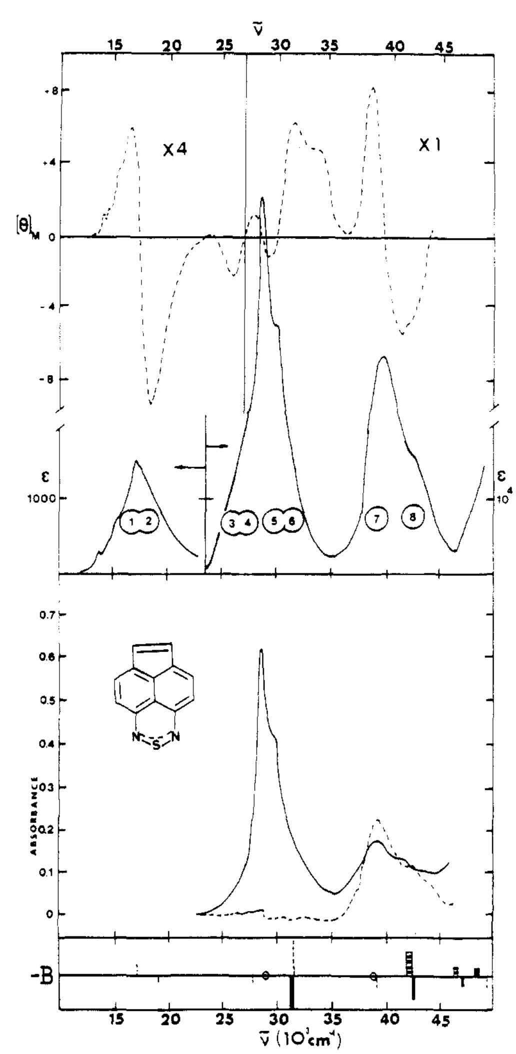

Figure 2. Acenaphtho[5,6-*cd*][1,2,6]thiadiazine (**2**): top, MCD (B terms in units of $10^{-3}\,\beta_e D^2/\mathrm{cm}^{-1}$) overlayed with absorption spectrum; middle, polarized spectra obtained from measurement of LD in stretched polyethylene sheets [dashed, short-axis (y) polarized absorption; full, long-axis (z) polarized absorption]; bottom, calculated. Calculated $-B$ values are indicated by the length of the bars in units of $10^{-3}\,\beta_e D^2/\mathrm{cm}^{-1}$ ($|B| < 10$, short; $10 < |B| < 30$, medium; $100 < |B| < 200$, long); calculated oscillator strengths are indicated by their grades of thickness, a circle indicating extremely weak. Calculated polarization directions are given as follows: y, dotted bar; z, heavy bar.

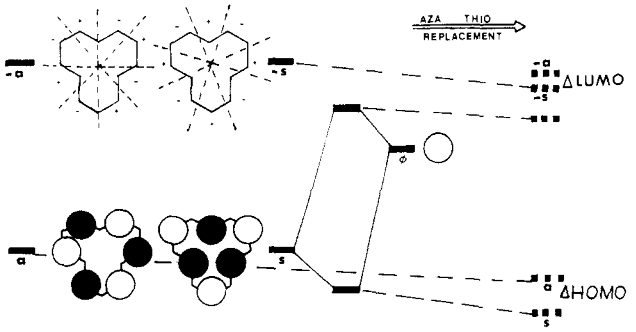

Figure 3. Effect of cross-linking and aza and thio replacement upon the molecular orbitals of the [12]annulenide dianion.

The agreement of the experimental excitation energies, relative intensities, polarizations, and MCD signs with the values calculated from the PPP model is excellent up to quite high energies. Although this is satisfying, it actually produces little qualitative insight into the origin of the

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(8) Castellan, A.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6824.

(9) Jørgensen, N. H.; Pedersen, P. B.; Thulstrup, E. W.; Michl, J. *Int. J. Quantum Chem.* **1978**, *12S*, 419.

Table I. Comparison of Experimental and Calculated Electron Transitions of 2 and 3

compd	parameter	transition[a] 1	2	3	4	5	6	7	8
2	exptl *E*	16.8 (m)	18.5 (w)	26.0 (w)	27.8 (w)	29.2 (s)	31.5 (m)	38.5 (s)	42.5 (m)
	pol	nd	nd	*y*	*y*	*z*	*z*	*y*	*z*
	B	–	+	+	–	+	–	–	+
	calcd *E*	16.6 (w)	18.9 (vw)	27.7 (w)	29.1 (vw)	31.5 (s)	31.6 (w)	42.0 (s)	42.6 (m)
	pol	*y*	*z*	*y*	*z*	*z*	*y*	*y*	*z*
	B	–	+	+	+	+	–	–	+
3	exptl *E*	14.0 (w)	24.7 (m)[b]	28.5 (m)	30.5 (m)	36.0 (w)	38.8 (s)	43.2 (s)	47.0
	pol	nd	*z*	*y*	*z*	*y*	*z*	*y*	nd
	B	+	+	+	–	–	–	+	–
	calcd *E*	11.8	27.2 (m)	28.3 (m)	29.0 (w)	38.1 (w)	38.9 (s)	44.7 (s)	49.5 (s)
	pol	*y*	*z*	*y*	*z*	*y*	*z*	*y*	*y*
	B	+	+	+	–	–	+	+	–
3	exptl[c] *E*	14.7	24.7	27.9	30.8		38.5	42.7	
	pol		*z*	*y*	*z*		*z*	*y*	
	calcd[c] *E*	11.9	25.0	27.3	30.3		35.5	36.8	
	pol	*y*	*z*	*y*	*z*		*z*	*y*	

[a] s = strong, m = medium, w = weak, vw = very weak, and nd = not determined. [b] The position of the apparent origin. [c] Data taken from ref 2e.

observed quantities. In particular, it is interesting to ask whether it is possible to understand the origin of the MCD signs in simple terms. This might be possible if the electronic states of 2 and 3 can be related to the L and B states of their perimeters, since the perimeter model is known to provide a simple rationalization of MCD signs of the low-energy L bands and often even the high-energy B bands in systems derived from (4*N* + 2)-electron annulenes.[4] It should be noted that by definition the sign of the *B* term of a transition is opposite the sign of its peak in the MCD spectrum.

(1) Acenaphtho[5,6-*cd*][1,2,6]thiadiazine (2). This molecule can be derived from the 14-electron [13]-annulenide anion by introducing an internal ethylene bridge to produce the acephenalenide anion 4 in a manner quite analogous to the formal construction of pyrene from [14]annulene[4a] and by subsequently replacing a three-carbon unit by the sulfur diimide moiety. A diagram showing the correlation of Hückel MO's during this process is shown in Figure 1. The frontier orbitals of the perimeter are labeled +s, +a, –s, and –a, where the plus sign indicates a bonding and the minus sign an antibonding MO and where s indicates a symmetric and a an antisymmetric MO relative to the vertical symmetry plane in Figure 1.

The orbitals +a and –a have inappropriate symmetry for interaction with the ethylene cross-link. However, +s strongly interacts with the LUMO of ethylene, and –s similarly interacts with its HOMO. The resulting ordering of the energy levels is +s, +a, –a, –s. Inspection of the symmetry-determined positions of nodes in the [13]-annulenide anion or of the numerical values of MO coefficients suggests that the bridge oribitals should interact equally strongly with the +s and –s orbitals of the perimeter, so that ΔHOMO ≃ ΔLUMO (ΔHOMO is the energy splitting of orbitals +s and +a and ΔLUMO that of orbitals –s and –a). Anion 4 is therfore a representative of the class of single-soft MCD chromophores, in which the usually large μ^+ contributions to the MCD *B* terms approximately vanish (exactly if ΔHOMO = ΔLUMO), leaving only the μ^- contributions, which are very weak in the case of the L bands and somewhat stronger for the B bands.[4b] Perturbations which destroy the equality of ΔHOMO and ΔLUMO introduce the potentially strong μ^+ contributions and in this manner dominate the MCD spectrum of the perturbed molecule.

If thio and aza substitution are considered as additional perturbations of 4, the MO energies are predicted to decrease. To first order, the decrease is proportional to the square of the coefficients at the site of replacement. The orbitals –a and +a are expected to drop somewhat (large white arrows down in Figure 1) because of the electro-

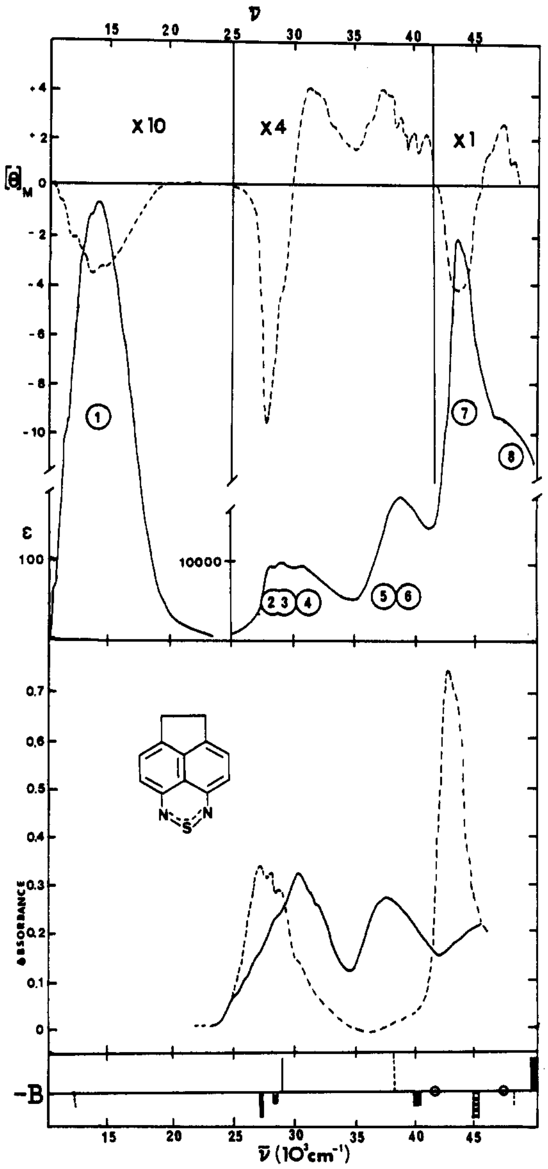

Figure 4. 6,7-Dihydroacenaphtho[5,6-*cd*][1,2,6]thiadiazine (3). See the caption to Figure 2 (|*B* < 4, short; 4 < |*B*| < 9, medium; 9 < |*B*| < 20, long).

negative nitrogen replacement at positions of high electron density in the [13]annulene perimeter, but they have a node at the position where sulfur occurs. The orbitals −s, and to a somewhat smaller degree +s, are expected to drop in energy much more because of the combined perturbation from both sulfur and nitrogen. The replacement of carbon by sulfur is particularly effective since the π-symmetry electrons in an AO of neutral sulfur are held much more firmly than they are in the analogous AO of the CH^- group. The results of the shifts are the reordering of energy levels to +s, +a, −s, −a, in agreement with PPP calculations, and the prediction that ΔHOMO < ΔLUMO. For such a case, the simple perimeter model predicts signs of μ^+ contributions to the *B* terms as −, +, −, and + for the L_1, L_2, B_1, and B_2 transitions, i.e., in the order of increasing energy. For the [14]annulenide perimeter, a weakly negative μ^- moment is expected,[4b] and therefore the weak μ^- contributions to the L bands and the stronger μ^- contribution to the B bands should have the sign sequence +, −, +, − in the order of increasing energy. Since in this case the bridge incorporated into the annulene perimeter is not charged, no orbitals are introduced by the perturbation between the frontier orbitals of the perimeter, and one can confidently expect to identify the two oppositely polarized L transitions as the lowest two observed ππ* transitions. The identification of the two B states may prove more difficult if they mix strongly with higher energy configurations not considered in the simple perimeter model. Naively, one expects to observe them as the next two highly intense transitions of opposite polarizations.

The experimental MCD, LD, and electronic absorption spectra for **2** are shown in Figure 2. The spectrum is richly populated with transitions as the MCD curve and PPP calculations indicate, illustrating the value of MCD spectroscopy in identifying overlapping transitions in electronic absorption bands. The identification of the L_1 transition with the MCD band near 16 900 cm^{-1} with a negative *B* term (positive MCD) and of the L_2 transition with the next MCD band near 18 500 cm^{-1} with a positive *B* term (negative MCD) is straightforward. One suspects that the two B transitions overlap and are centered about 30 000 cm^{-1} where a strong *z*-polarized transition in the LD spectrum is accompanied by a weak *y*-polarized component. The presence of at least two transitions in this region is much clearer in the MCD spectrum; the most likely number is four.

Inspection of PPP wave functions confirms the assignment of transitions L_1 and L_2 as the first two ππ* transitions 1 and 2 in Figure 2. Our attempts to determine their polarizations from LD measurements were unsuccessful due to limited solubility of **2** in polyethylene and the weakness of the transitions. The PPP results further suggest that the calculated transitions 3 and 5, assigned to the observed transitions 3 and 5 in Figure 2, correspond to the B_1 and B_2 transitions. While the MCD signs of the two L bands are exactly as predicted by the simple perimeter model, the severe overlap of transitions 3–6 makes the analysis for the *B* terms of the B_1 and B_2 bands difficult. The B_1 transition (3 in Figure 2) is of medium intensity, comparable with L_1 and L_2, and in the PPP description corresponds to the excitation s → −a (short axis polarized). Its origin lies near 24 000 cm^{-1} and is positive in the MCD spectrum as expected from the perimeter model. However, it is very weak, and most of the MCD curve in the region of transition 3 is actually negative. The B_2 transition (5 in Figure 2) is long-axis polarized and quite intense. Its PPP description is an a → −a excitation with a strong in-phase admixture of s → −s, enhancing the intensity (the out-of-phase combination, in which s → −s dominates, corresponds to the weaker transition L_2). According to the perimeter model, the mutual magnetic mixing of B_1 and B_2 should dominate their *B* terms, providing the former with a μ^+ contribution of a negative sign and the latter with a μ^+ contribution of a positive sign, since ΔHOMO < ΔLUMO. By themselves, these contributions would produce a positive MCD sign for B_1 and a negative for B_2. However, the frequently weaker μ^- contributions to the magnetic B_1–B_2 mixing have signs opposed to those of the μ^+ contributions, so that the observed effects could easily be rather weak. In the present case, the presence of the nearly degenerate additional transitions 4 and 6, which originate in excitations involving orbitals other than the four considered in the simple model, is likely to play a significant role. In particular, it appears from the PPP calculation that the *B* term of transition 5 is determined primarily by the magnetic mixing 5–6, so that the perimeter model no longer is applicable. The full π-electron calculation, which considers all possible magnetic mixings, produces the correct signs for these transitions. In this case, then, the simple perimeter model is successful for the lowest two or possibly three ππ* transitions.

(2) 6,7-Dihydroacenaphtho[5,6-*cd*][1,2,6]thiadiazine (3). In this case, we proceed similarly as done previously for pleiadiene[3b] and aceheptylene.[3d] We construct the orbitals of the isoelectronic phenalenide anion (**5**) from those of the 14-electron [12]annulenide dianion and that of methyl cation located in the center of the ring. A diagram exhibitng the correlation of Hückel MO's is shown in Figure 3. On an orbital energy scale, the nonbonding methyl orbital φ will insert itself between the bonding +s, +a and antibonding −s, −a pairs of annulene orbitals. This nonbonding orbital has minimal first-order effects on orbitals +a, −a, and −s which have the wrong symmetry for interaction. However, it mixes strongly with the orbital +s. The in-phase combination produces a new MO of lower energy and causes a separation of the original degenerate HOMOs. Thus, ΔHOMO > 0 = ΔLUMO, and anion **5** therefore belongs to the category of positive −hard MCD chrmophores.[4] The out-of-phase combination of +s and φ creates a new MO whose energy lies between those of the degenerate LUMO set and of the original HOMO set. We refer to this orbital, absent in the MO scheme of the unperturbed perimeter, as the "intruder" orbital. The presence of the intruder orbital, which is relatively low lying and vacant in the ground state, produces an opportunity for low-energy excitations which have no counterpart in the spectrum of the orignal perimeter, as we shall see below.

An additional perturbation of the perimeter occurs when three carbon atoms are replaced by the sulfur diimide bridge. The aza and thio substitution will lower the energy of each Hückel MO. The degree of the lowering can be estimated by calculating the square of the AO coefficient in the MOs of **5** or, more simply, in those of the original [12]annulene at the site where the aza or thio replacements occur. Inspection of the symmetry-determined nodal properties of these MOs or, alternatively, perusal of a tabular listing of the coefficients[10] produces the qualitative conclusion about the ordering of the energy levels shown in Figure 3. In particular, the energy of −a is lowered less than the energy of −s because the sulfur replacement occurs at a node in −a. However, the qualitative result is still ΔHOMO > ΔLUMO, and **3** is positive–hard, like the

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[10] Heilbronner, E.; Straub, P. A. "Hückel Molecular Orbitals, HMO"; Springer-Verlag: New York, 1966.

parent phenalenide anion. Relative to the effect of the sulfur diimide bridge, the effect of the saturated ethano substituent can safely be neglected.

For positive–hard chromophores, the simple theory predicts large μ^+ contributions to the B terms with signs +, −, +, and −, respectively, for the L_1, L_2, B_1, and B_2 transitions. The μ^- contributions are expected to be negligibly small in the case of the 14-electron 12-atom perimeter.[4b]

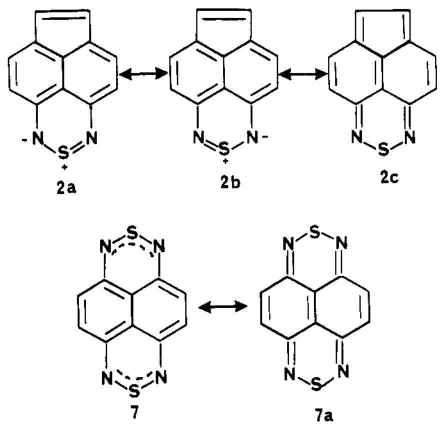
Correlation with the experimental signs requires the identification of the two relatively weak L and two relatively strong B transitions. Ordinarily this is quite easy, but the presence of the intruder orbital complicates the situation. Since it represents the lowest vacant orbital, one suspects that an excitation of an electron from the HOMO into it will represent the lowest energy excitation. This would then be an "intruder" excitation rather than one of the four for which the above sign predictions hold. The suspicion is strengthened by comparison with the analyses available for pleiadiene[3b] and aceheptylene.[3d] Indeed, inspection of the PPP wave functions leaves no doubt that transition 1 in Figure 4 corresponds to such an excitation. There is relatively little configuration mixing, and these results make it quite clear that calculated transitions 1, 4, 5, and 6, which correspond to experimental transitions 1, 4, 5, and 6, are due to electron transitions from the top four MOs, respectively, into the intruder orbital. Transitions 2 and 3, polarized along z and y, respectively, correspond to the L_1 and L_2 bands, and calculated transitions 8 and 11, assigned to the observed transitions 7 and 8, correspond to the B_1 and B_2 bands. It is now clear that the observed MCD signs of transitions L_1, B_1, and B_2 agree with expectations for a positive–hard chromophore. That of transition L_2 is hard to determine due to excessive overlap with the intruder transition 4. The MCD signs calculated by the PPP method are available for all four perimeter transitions and agree with the simple perimeter model except in the case of L_2, which appears to be affected by magnetic mixing with the nearby intruder transition 4. Still, on consideration of how much 3 has been perturbed relative to the parent [12]annulene dianion or even 5, the performance of the simple model is remarkable.

(3) Bonding in Condense Thiadiazines. It is of some interest to note the values of calculated bond orders for 1–3 and 6 shown in Chart I. Their interpretation is based on the assumption that 3d orbitals play a negligible role. This has been shown to be quite plausible in the case of 3 by Bartetzko and Gleiter.[2e] The π bond order that we calculate for the isolated sulfur diimide group in 6 is 0.67 and this is comparable to that found for the N–S bond in 3. The π bond order for 2 is 0.54 for the N–S bond, and the peri bridge shows a bond order of 0.74, about 10% less than that in acenaphthylene (0.85). This suggests that resonance structure 2c is a significant contributor to the ground state of 2. This is also reflected in the higher C–N π bond order for 2 as compared to that for 3. This result is consonant with the conclusion reached in previous studies on naphtho[1,8-*cd*:4,5-*c′d′*]bis[[1,2,6]thiadiazine][2c] (7, Chart II) which make it abundantly clear that structure (7a) constitutes a major contributor to the description of the ground state.

Summary

The similarity of the solution absorption spectra of 2 and 3, particularly the presence of a visible band responsible for their color and well separated from stronger bands in the near-UV region, is only superficial. A more thorough characterization by means of MCD and LD spectroscopy and a theoretical analysis based on π-electron calculations and the simple perimeter model bring to light substantial differences between the two compounds. The fully unsaturated compound 2 is the simpler to understand. In terms of the perimeter model, its visible absorption is due to the superposition of the oppositely polarized L_1 and L_2 transitions, and the B_1 and B_2 transitions contribute to the very intense band near 30 000 cm^{-1}. The π system of the partially hydrogenated compound 3 is characterized by the presence of an "intruder" molecular orbital located between the highest two occupied perimeter orbitals and the lowest two empty perimeter orbitals. The presence of the intruder orbital, which represents the LUMO of 3, causes the appearance of low-energy excitations which lie outside the scheme of the L and B perimeter states. The visible band of 3 is due to the lowest of these "intruder" transitions; several others have been identified. The L_1 and L_2 transitions lie in the near-UV (30 000 cm^{-1}), and the B_1 and B_2 transitions are assigned to the very intense band near 45 000 cm^{-1}.

Chart II


2a 2b 2c

7 7a

The polarizations and the MCD signs of the L and B bands are in reasonable though not perfect agreement with expectations based on the simple perimeter model. Also, in this respect, the two compounds differ significantly. The MCD sign-determining quantity, ΔHOMO − ΔLUMO, vanishes for the unperturbed perimeters ([13]annulenide anion and [12]annulene dianion). It is still very nearly zero in the parent anion of 2, the acephenalenide anion, but it is large and positive in the parent anion of 3, the phenalenide anion, as is readily rationalized by using Hückel MO correlation diagrams. Thus, the former (2) is a single–soft[4b] and the latter (3) a positive–hard[4b] MCD chromophore. It is only the additional perturbation of the sulfur diimide moiety which causes ΔHOMO < ΔLUMO in 2 and thus leads to the correct prediction of its observed MCD signs; other replacement patterns on 4 and/or further substitution on 2 have the potential of reversing the MCD signs, particularly for the L bands. To the contrary, the order ΔHOMO > ΔLUMO inherent to 5 is not changed by the sulfur diimide group and accounts well for the observed MCD signs of 3. The MO energy ordering will be quite difficult to change by further perturbations, as is characteristic of a hard chromophore.

It is perhaps no longer surprising that the PPP calculations account correctly for the energies, relative intensities, polarizations, and MCD signs of electronic transitions in molecules such as 2 and 3. However, it is still noteworthy to what degree the results, and in particular the MCD signs, can be understood by using the simple perimeter model, considering the magnitude of the perturbations required to convert the respective perimeter anions 2 and 3. The unusual sulfur diimide moiety appears to pose no special problems.

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Electrochemistry of Carbonium Ions in Acidic Media. 1. Triphenylmethyl Ion in Aluminum Chloride Containing Melts

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The electrochemistry of the triphenylmethyl carbonium ion (1) has been studied in a room-temperature aluminum chloride containing melt. Formation of 1 is dependent on the acidity or pCl of a molten aluminum chloride/*n*-butylpyridinium chloride (1:1) binary mixture. The equilibrium constant for reaction 1 is 20.4 ± 0.3 mol L^{-1} at 40 °C as determined by spectroscopic techniques. Formation of 1 from triphenylmethyl chloride is too slow to quantitatively determine a rate constant (k_f) by conventional electrochemical techniques. Cyclic voltammetric and controlled-potential coulometric data reveal that 1 is reduced in an one-electron process to a triphenylmethyl radical (2). Formation of 2 in the $AlCl_3$ melt is verified by ESR spectroscopy. Dimerization of 2 produces an electrochemically oxidizable form of 1-(diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene (3); the rate constant for the dimerization of 2 is $1.33 \pm 0.08 \times 10^3$ l mol^{-1} s^{-1} at 40 °C. Workup of an exhaustively electrolyzed solution of 1 in the melt produces [4-(diphenylmethyl)phenyl]triphenylmethane, which is the result of proton isomerization of 3.

Molten salts, in particular tetrachloroaluminate melts, have been found to be useful solvents for organic electrochemical studies due to their totally aprotic and anhydrous properties.[1] Most recently aluminum chloride-/alkylpyridinium halide binary mixtures have been shown useful for such studies due to liquidus temperatures close to ambient temperatures.[2-4] This laboratory has recently become interested in the aluminum chloride/*n*-butylpyridinium chloride ($AlCl_3$/BPC) mixtures. Spectroscopic studies indicate that the predominant aluminum species in the $AlCl_3$/BPC melts are $AlCl_4^-$ and $Al_2Cl_7^-$, the relative ratio of which is dependent upon the composition.[5] The acid–base chemistry of these melts is of particular interest and can be described by the reaction $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, with an equilibrium constant of 3.8×10^{-13} at 30 °C.[6] By varying the melt composition from 0.75:1 to 2:1 $AlCl_3$/BPC, the pCl of the melt can be varied from 0 to 15. Thus, the acidity range in these melts compares favorably with that found in conventional aqueous chemistry.

Several studies involving the electrochemical oxidation of aromatic amines and polycyclic aromatic hydrocarbons indicate improved stability of radical cations in the $AlCl_3$-containing melts.[2,3,7,8] In addition, recent work in this laboratory shows improved stability for monoamine dications as well as radical cations in the $AlCl_3$/BPC melt.[9] The most plausible explanation for this improved stability of cationic species is the absence of nucleophiles of appreciable strength in these $AlCl_3$ melts. It was therefore decided to take advantage of this property in the preparation and subsequent electrochemical study of carbonium ions in the $AlCl_3$ melt. The approach used in this laboratory included the generation of carbonium ions by the reaction $RCl + Al_2Cl_7^- \rightleftarrows R^+ + 2AlCl_4^-$, which can be controlled by adjustment of the pCl or $AlCl_3$ composition of the melt. The initial results of this approach for the generation of electroactive carbonium ions are presented here. Electrochemical studies on the triphenylmethyl carbonium ion in an $AlCl_3$/BPC melt are presented.

Experimental Section

Chemicals. Triphenylchloromethane (mp 110.5–111.5 °C) was prepared by reacting triphenylmethanol (Matheson) with freshly distilled acetyl chloride (Fisher) in benzene and was recrystallized from benzene.[10] 1-(Diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene (3) was obtained by reducing triphenylchloromethane with molecular silver:[11] For 3: ^1H NMR of ($CDCl_3$) δ 6.8–7.4 (20, aromatic), 5.8–6.4 (4, olefinic), 4.9 (1, methine); ^{13}C NMR ($CDCl_3$) 43.66, 62.44, 125.59, 126.05, 126.57, 127.67, 128.06, 130.27, 137.16, 141.44, 143.65, 146.64. [4-(Diphenylmethyl)-phenyl]triphenylmethane (4, mp 225–227 °C) was prepared by bubbling HCl in a benzene solution of 3.[12] For 4: ^1H NMR ($CDCl_3$) δ 7.0–7.5 (29, aromatic) 5.5 (1, aliphatic); ^{13}C NMR ($CDCl_3$) δ 56.33, 64.58, 125.79, 126.18, 127.28, 128.19, 129.36, 131.05, 141.19, 143.85, 144.63, 146.71.

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[1] M. Fleischman and D. Pletcher, *J. Electroanal. Chem.*, **25**, 449 (1970); H. L. Jones, L. G. Boxall, and R. A. Osteryoung, *ibid.*, 38, 476 (1972); K. W. Fong, J. Q. Chambers, and G. Mamantov, *ibid.*, 47, 81 (1973); V. P. Koch, L. L. Miller, and R. A. Osteryoung, *J. Org. Chem.*, **39**, 2416 (1974); D. E. Bartak and R. A. Osteryoung, *J. Electrochem. Soc.*, **122**, 600 (1975).

[2] J. Robinson and R. A. Osteryoung, *J. Am. Chem. Soc.*, **101**, 323 (1979).

[3] J. Robinson and R. A. Osteryoung, *J. Am. Chem. Soc.*, **102**, 4415 (1980).

[4] V. P. Koch, L. L. Miller, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **98**, 5277 (1976).

[5] R. J. Gale, B. Gilbert, and R. A. Osteryoung, *Inorg. Chem.*, **17**, 2728 (1978).

[6] R. J. Gale and R. A. Osteryoung, *Inorg. Chem.*, **18**, 1603 (1979).

[7] H. L. Jones and R. A. Osteryoung, *J. Electroanal. Chem.*, **49**, 201 (1974).

[8] H. L. Chum, V. P. Koch, L. L. Miller, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **97**, 3264 (1975).

[9] G. D. Luer and D. E. Bartak, in preparation.

[10] E. C. Horning, Ed., "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 841.

[11] M. Gomberg, and L. H. Cone, *Ber.*, **37**, 2034 (1904).

[12] H. Takeuchi, T. Nagai, and N. Tokura, *Bull. Chem. Soc. Jpn 44*, 753 (1971).

0022-3263/82/1947-1238$01.25/0