

with confidence that its unobserved third excited singlet state lies near $34\,000\text{ cm}^{-1}$, between the L_a and B_b bands. The existence of this state has been recently deduced from a study of azapyrenes,⁸ and may be of interest for interpretation of two-photon absorption work.

Similarly, our data also show quite unambiguously the presence of a transition near $40\,000\text{ cm}^{-1}$ (transition 5) in pyrene derivatives and, again by extrapolation, in pyrene itself. The existence of this weak transition has been suspected for some time¹⁵ and was substantiated also in our MCD study of azapyrenes.⁸ About four weak transitions are calculated in this region by the PPP method.

Finally, and not surprisingly, our MCD data show that the absorption region of the B_a transition is composite and contains several transitions. These may correlate with some of the four mentioned above, with another four or so calculated at somewhat higher energies, or with transitions into states of partially doubly excited nature which do not appear in the simple PPP approximation used here.

Conclusions

The simple theory of parts 1–3^{4–6} accounts well for the qualitative features of the MCD spectrum of pyrene and, even semiquantitatively, for the substituent effects on the L_b , L_a , and B_b bands. The experimental data permit a conclusive identification of two new transitions near $34\,000\text{ cm}^{-1}$ and near $40\,000\text{ cm}^{-1}$ in pyrene derivatives and, by extrapolation, in pyrene itself, as well as a more tentative identification of several new excited states at higher energies.

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Magnetic Circular Dichroism of Cyclic π -Electron Systems. 14.¹ Derivatives of Azulene

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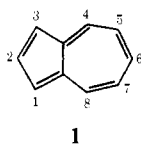
Abstract: Magnetic circular dichroism of five alkylazulenes is reported. Analysis of the results leads to a reassignment of the sign of the B term of the fourth singlet–singlet transition (B_a) and confirms the presence of two new excited states at $40\,000$ and $46\,000\text{ cm}^{-1}$. Standard PPP calculations are in good agreement with the results and indicate that the state at $40\,000\text{ cm}^{-1}$ is predominantly doubly excited (HOMO,HOMO \rightarrow LUMO,LUMO). Regardless of the position of alkyl substitution, the MCD signs agree with those of azulene itself and with the theory of parts 1–3. The region of the L_a band is the most sensitive to perturbation, as expected for weak substituents on a chromophore which is intermediate between positive-hard and even-soft.

Introduction

MCD properties of alkyl derivatives of azulene are of interest for testing the simple qualitative theory of MCD signs of transitions involving the L and B states of a π -electron perimeter, presented in parts 1–3 of this series.^{3–5} This theory introduced the distinction between hard ($\Delta\text{HOMO} \neq \Delta\text{LUMO}$) and soft ($\Delta\text{HOMO} = \Delta\text{LUMO}$) MCD chromophores, based on their expected response to perturbations [$\Delta\text{HOMO} = |E(\mathbf{a}) - E(\mathbf{s})|$ and $\Delta\text{LUMO} = |E(-\mathbf{a}) - E(-\mathbf{s})|$], where the MO's \mathbf{a} , \mathbf{s} , $-\mathbf{a}$, $-\mathbf{s}$ are derived from the four

frontier orbitals of the π -electron perimeter as described in more detail in parts 1–3^{3–5}]. The existence of several types of soft chromophores was predicted. In parts 4–14 of this series, we probe substituent effects on various kind of chromophores derived from an uncharged perimeter. The response of double-soft chromophores to mesomeric (E) and inductive (I) effects was discussed in part 4.⁶ The response of odd-soft chromophores was examined in parts 7,⁷ 8,⁸ 9,⁹ 10,¹⁰ 11,¹¹ 12,¹² and 13.¹ In parts 5¹³ and 6¹⁴ and in the present paper, we consider even-soft chromophores, and in the remainder of this series, we focus attention on hard chromophores.

Azulene (**1**) can be formally derived by an even perturbation of [10]annulene, namely by introduction of a cross-link between atoms ν and $\nu + 4$. Properties of the perimeter orbitals make it clear¹⁵ that the cross-link raises the energy of orbitals



\mathbf{a} and $-\mathbf{a}$ which have a node across it and lowers the energy of \mathbf{s} and $-\mathbf{s}$, which do not, resulting in the orbital ordering \mathbf{s} , \mathbf{a} , $-\mathbf{s}$, $-\mathbf{a}$. Since in [10]annulene orbital \mathbf{s} is paired with $-\mathbf{s}$, the shifts induced by the perturbation in both of them are the same to the first order, and similarly for orbitals \mathbf{a} and $-\mathbf{a}$. To the first order, then, $\Delta\text{HOMO} = \Delta\text{LUMO}$, and azulene should be an even-soft chromophore. The cross-link is a rather strong perturbation, though, and a full Hückel or PPP calculation shows that $\Delta\text{HOMO} - \Delta\text{LUMO}$, though not large, is distinctly positive. Therefore, one can expect azulene to be intermediate between an even-soft chromophore and a positive-hard chromophore. It should behave like a hard chromophore with respect to weak perturbations, such as the alkyl substitution investigated here, but it should be possible to change its MCD signs, most easily that of the L_a band, by introduction of stronger substituents, and we shall make some specific predictions of such sign changes.

The excited singlet states of **1** have been the subject of considerable attention in the past. A summary of previous work and assignments has appeared recently¹⁶ and will not be repeated here. The generally accepted assignments of the L and B transitions in **1** are as follows: L_b , near 14 500 cm^{-1} , weak and short-axis polarized; L_a , near 28 000 cm^{-1} , medium intensity (mostly borrowed by vibronic interaction with B_a) and long-axis polarized; B_b , near 33 500 cm^{-1} , medium intensity and short-axis polarized; B_a , near 35 000 cm^{-1} , strong and long-axis polarized.

Previous reports from this laboratory^{16,17} described the MCD spectrum of **1**. The signs of the first (+), second (-), and third (+) B terms were those expected from standard PPP calculations of the type described in part 4,⁶ but the agreement of signs at higher energies was poor. In the region of the fourth absorption band, the shape of the MCD curve was very different from the shape of the absorption curve. It was proposed that the fourth MCD band is negative and overlaps with one or more previously unidentified transitions. It was further pointed out that the second MCD band shows clear signs of strong vibronic interaction with the fourth transition, using totally symmetric vibrations, but it was felt that spectral resolution was insufficient for a detailed analysis. Such an analysis was subsequently proposed by Dekkers and Westra,¹⁸ and the MCD curve of **1** was also reported by Tajiri and Hatano.¹⁹

We now report MCD spectra of a series of alkyl derivatives of **1**, which allow us not only to probe the response of a nearly even-soft chromophore to very weak perturbations but also to shed new light on some of the problems noted earlier.¹⁶ The new spectra make it clear that the sign of the fourth MCD band in **1** actually is positive and thus agrees with previous PPP calculations, after all, and also with the simple model of parts 1-3.³⁻⁵ Finally, the data also confirm the presence of two new transitions near 40 000 and 46 000 cm^{-1} . Comparison with PPP calculations indicates that the first of these involves a predominantly doubly excited state.

Experimental Section

The samples were gifts from Professor K. Hafner (Technische Hochschule, Darmstadt), Professor C. Jutz (Universität München), and Dr. U. Müller-Westerhoff (IBM Research Laboratory, San Jose). They were chromatographed over alumina (grade I) with light pe-

troleum ether, recrystallized from methanol, or sublimed as required. Details of the measurements were given in part 4.⁶ The alkylazulenes will be referred to by symbols such as 6-Me-**1**, where Me = methyl, *i*-Pr = isopropyl, *t*-Bu = *tert*-butyl, and the positions of substitution are indicated.

Calculations

A calculation for **1** using selected singly and doubly excited configurations were performed as in ref 16 and 17 (SECI-1) but using values for resonance integrals $\beta_{\mu\nu}$ (in eV) and electron repulsion integrals $\gamma_{\mu\nu}$ (in eV) which had been proposed²⁰ for use with large-scale configuration interaction:

$$\beta_{\mu\nu} = -2.6 \exp[0.335(p_{\mu\nu} - 2/3)]$$

$$\gamma_{\mu\nu} = 14.4[1 - 0.18 \exp(-3.2r_{\mu\nu})]/(1.328 + r_{\mu\nu})$$

Bond lengths for neighbors $r_{\mu\nu} = 1.517 - 0.18p_{\mu\nu}$ (Å) were iterated to self-consistency with bond orders $p_{\mu\nu}$. The automatic configuration selection procedure chose 17 singly excited and 101 doubly excited configurations to produce what we expect to be a good approximation to an all-singles plus all-doubles calculations.

Results

The results are shown in Figures 1-5. Figure 6 shows the previously published¹⁶ spectrum of **1** for comparison, along with the new calculations. The spectroscopic information derived from the spectra is summarized and compared with calculations in Table I. No reliable determination of the numerical values of purely electronic B terms appears possible due to excessive band overlap and/or vibronic mixing. The absorption spectra as well as MCD spectra of all six compounds are very similar, and there is no difficulty in correlating transitions from one compound to the next, as shown in the figures. The degree of vibronic activity of the second transition and the extent to which it produces a positive MCD signal are a sensitive function of substitution. As before,¹⁶ we feel that the available resolution is insufficient to analyze the very complicated vibrational fine structure of this transition.

The structured negative MCD band of the short-axis-polarized third transition is pronounced in all alkylazulenes and corresponds to only a weak shoulder or peak in absorption. This is a nice example of different relative intensities in MCD and absorption spectra, helpful for identification of new transitions.

Discussion

Spectral Assignments. The assignment of the first four transitions as L_b , L_a , B_b , and B_a , respectively, is without

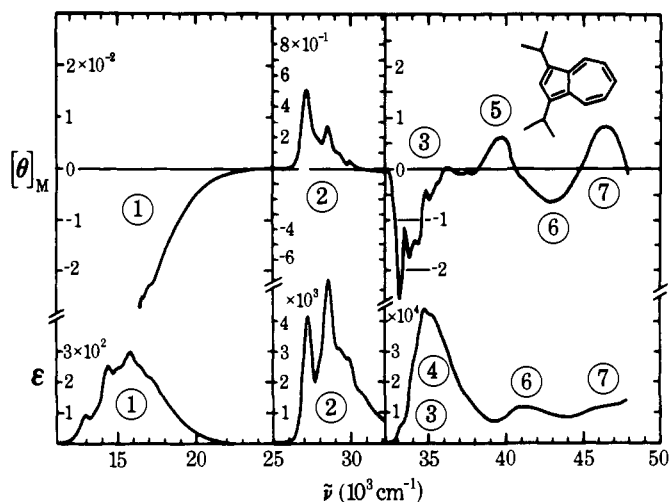


Figure 1. 1,3-Diisopropylazulene spectra: bottom, absorption; top; MCD ($\text{deg L mol}^{-1} \text{m}^{-1} \text{G}^{-1}$).

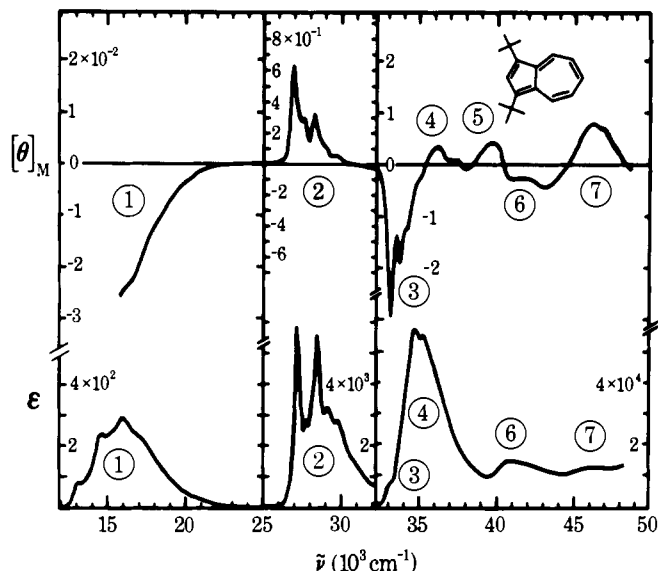


Figure 2. 1,3-Di-*tert*-butylazulene. See caption to Figure 1.

problems. The two transitions at $42\,000\text{ cm}^{-1}$ (short-axis polarized, positive B term, no. 6) and at $51\,400\text{ cm}^{-1}$ are the only previously known higher excited singlet states of **1**. The MCD spectrum of **1** (Figure 6) does not follow its absorption spectrum above $35\,000\text{ cm}^{-1}$ and it was proposed¹⁶ that additional transitions, not obvious in absorption, are probably present. Comparison of Figures 1–6 now shows with much greater certainty that two new states are indeed present. One of these, near $40\,000\text{ cm}^{-1}$, is positive in MCD (negative B term, no. 5; 6-Me-**1**, 1,3-*i*-Pr-**1**, 1,3-*t*-Bu-**1**) and has no counterpart in absorption. The other, no. 7 near $46\,000\text{ cm}^{-1}$, is also positive in MCD (1,3-*i*-Pr-**1**, 1,3-*t*-Bu-**1**, 4,8-Me-**1**, 4,6,8-Me-**1**, and in several instances appears as an indistinct shoulder in absorption. The PPP results (Table I) suggest strongly that the $40\,000\text{-cm}^{-1}$ state contains a large contribution ($\sim 60\%$) from the doubly excited configuration HOMO,HOMO \rightarrow LUMO,LUMO. This is physically reasonable considering that the single HOMO \rightarrow LUMO excitation lies at $15\,000\text{ cm}^{-1}$. Similar doubly excited states had been previously found in two other polycyclic hydrocarbons, pleiadene²¹ and acenaphthylene,²² and states of this type are of considerable interest in the photochemistry²³ and in spectroscopy²⁴ of linear polyenes.

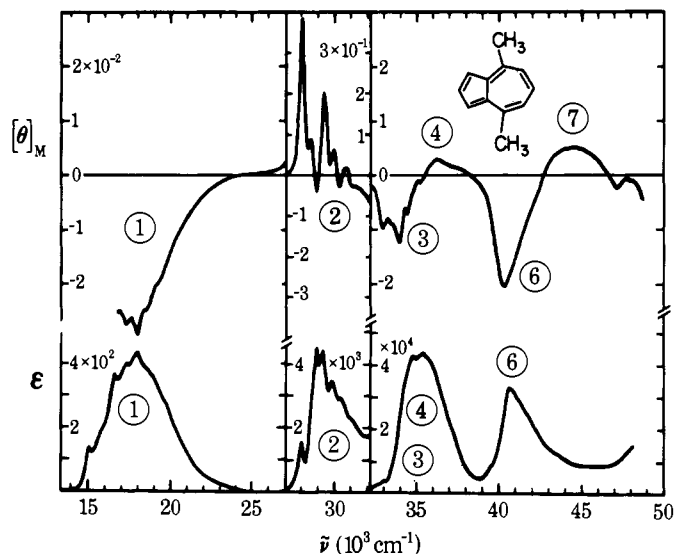


Figure 3. 4,8-Dimethylazulene. See caption to Figure 1.

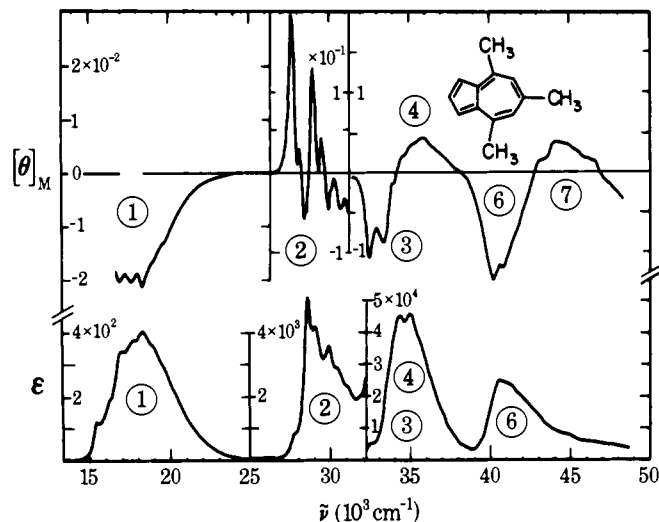


Figure 4. 4,6,8-Trimethylazulene. See caption to Figure 1.

MCD Signs. Inspection of the figures leaves no doubt about the signs of most of the B terms (1,3,6, positive; 2,5,7, negative). Only the negative sign which we now assign to the fourth B term (B_a) deserves additional comment, since we previously stated that it was positive.¹⁶ The reason for this reversal of opinion is that comparison of Figures 1–6 now makes amply clear what was not previously obvious to us from Figure 6 alone: there is a great reduction in the negative MCD intensity associated with the third transition as one reaches the origin of the fourth one and also beyond, plus a positive peak at higher wavenumbers, where the weak fourth MCD band finally prevails over the tail of the strong third MCD band. Similar difficulties in sign assignment are likely to be encountered generally in the interpretation of spectra which contain overlapping positive and negative peaks, such as MCD and CD.

The signs of $B(L_b)$ (weakly positive), $B(B_b)$ (positive), and $B(B_a)$ (negative) agree with expectations of the simple theory^{4,5} for μ^- contributions to the MCD of an even-soft chromophore. Since **1** is intermediate between even-soft and positive-hard ($\Delta\text{HOMO} > \Delta\text{LUMO}$), positive contributions to $B(L_b)$ and $B(B_b)$ and negative contributions to $B(L_a)$ and $B(B_a)$ are expected from the μ^+ terms. The outcome is an unequivocal prediction of just the observed signs for all four bands.

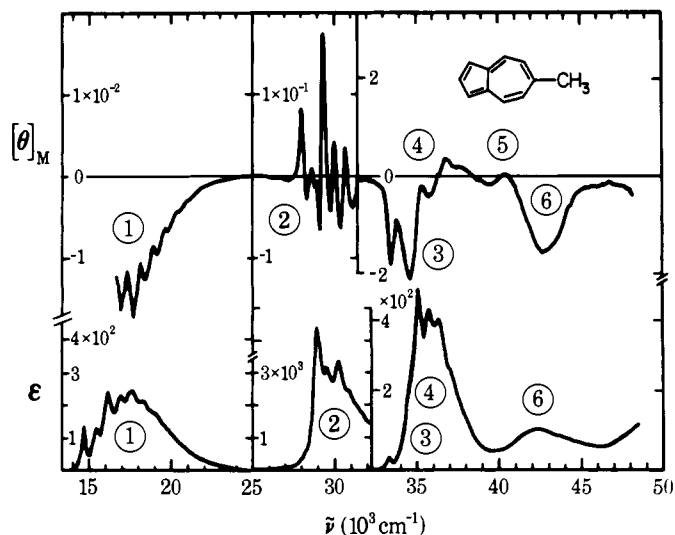


Figure 5. 6-Methylazulene. See caption to Figure 1.

Table I. Electronic Transition Energies in Alkylazulenes^a

	transition									
	1	2	3	4	5	6	7	8		
Experimental Results										
pol, sign of <i>B</i>	<i>y</i> , +	<i>z</i> , -	<i>y</i> , +	<i>z</i> , -	-	<i>y</i> , +	-			
int	w	m	m	s	w	m	m	s		
1 ^b	14.5	28.0	33.5	35.0	~40.5	42.0		51.4		
1,3- <i>i</i> -Pr- 1	13.0	27.1	33.2	35.0	40.0	41.2	~46.1			
1,3- <i>t</i> -Bu- 1	12.9	27.0	33.3	34.9	39.7	~41.2	~46.1			
4,8-Me- 1	15.1	28.0	32.9	34.8		40.7	44.4			
4,6,8-Me- 1	15.5	27.8	32.6	34.4		40.5	44.4			
6-Me- 1	14.7	27.2	33.3	35.1	40.0	42.4				
Calculated ^c for 1										
en	17.7	28.9	35.0	36.4	44.8	45.3	46.0	47.4	49.2	50.9
<i>f_r</i>	0.014	0.006	0.054	0.83	0.29	0.027	0.31	0.012	0.020	0.34
<i>f_p</i>	0.006	0.002	0.044	0.62	0.22	0.018	0.25	0.010	0.015	0.25
pol	<i>y</i>	<i>z</i>	<i>y</i>	<i>z</i>	<i>z</i>	<i>y</i>	<i>y</i>	<i>z</i>	<i>y</i>	<i>z</i>
<i>B</i>	0.17	-0.50	3.3	-2.9	-2.9	-10.0	17.5	-1.4	-4.0	
conf	1 → -1	1 → -2, 2 → -1	2 → 2	1 → -2, 2 → -1	1,1 → -1,-1; 4 → -1	1 → 3, 1,1 → -1,-2	3 → -1			

^a 0-0 transitions, in units of 1000 cm⁻¹. ^b From ref 16, using presently proposed interpretation of the short-wavelength region. ^c Present calculation (PPP-SECI-1). *f_r* and *f_p* are oscillator strengths from dipole length and dipole velocity formulas, respectively.

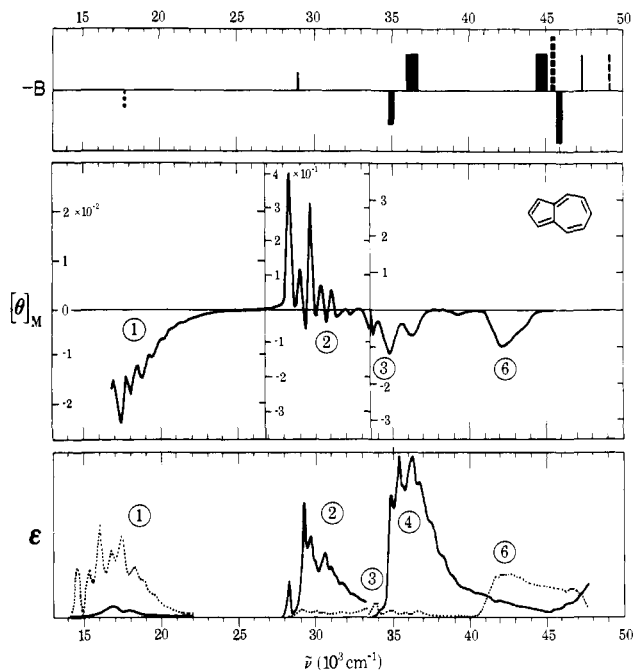


Figure 6. Azulene:¹⁶ bottom, polarized absorption (77 K, stretched polyethylene) with the full (dashed) line indicating long axis (short-axis) polarization; center, MCD spectrum (deg L mol⁻¹ m⁻¹ G⁻¹); top, SECI-1 calculation with the full (dashed) line indicating long-axis (short-axis) polarization. Oscillator strengths *f* (dipole length) are shown: thin lines, *f* ≤ 0.02; medium lines, 0.02 < *f* ≤ 0.2; thick lines, *f* > 0.2. Values of -*B* in units of 10⁻³ β_e D²/cm⁻¹ are indicated by the length of the lines: short, |*B*| ≤ 1; medium, 1 < |*B*| ≤ 10; long, |*B*| > 10.

The ΔHOMO-ΔLUMO difference is relatively small but nonzero, so that one can expect weakly perturbing substituents such as alkyl to leave the signs of the *B* terms unchanged. This is indeed observed (Figures 1-6) and distinguishes clearly the only nearly soft MCD chromophore, **1**, from really soft MCD chromophores such as naphthalene⁸ and anthracene,¹¹ in which already alkyl substitution has considerable and sometimes dramatic effects.

According to the simple model,^{4,5} the one band among the L and B bands of an even-soft chromophore which should show the most sensitivity to substituent effects is L_a, since it contains

no inherent μ⁻ contribution. Closer inspection of the figures shows that this is indeed the case. In 1,3-*t*-Bu-**1** and 1,3-*i*-Pr-**1**, *B*(L_a) is quite distinctly more negative than in **1**, and the band shows no evidence of vibronic effects. In 4,8-Me-**1**, *B*(L_a) is quite similar to that in **1**, perhaps slightly less negative, but in 4,6,8-Me-**1** and particularly in 6-Me-**1**, it is clearly less negative and the MCD curve integrates almost exactly to zero. The 0-0 transition is still positive in MCD, but much less so. Similar but less pronounced variations are observed in the size of *B*(L_b), but here the sign remains firmly positive, and the simple theory suggests that this is due to the inherent μ⁻ contribution.

In order to work out the expected effects of substituents on ΔHOMO and ΔLUMO, using first-order perturbation theory in the spirit of part 3,⁵ we list in Table II the squares of Hückel coefficients of azulene orbitals *a*, *s*, -*a*, and -*s*. An increase in the already positive value of ΔHOMO - ΔLUMO will add a further negative contribution to *B*(L_a) while a decrease in the magnitude of ΔHOMO - ΔLUMO will add a positive contribution to *B*(L_a). Thus, we expect substituents to contribute to *B*(L_a) as indicated in Table II. The signs shown in parentheses correspond to contributions which should be smaller, mostly because the normally weak effects of +E substituents on ΔHOMO and of -E substituents on ΔLUMO, which counteract their ordinarily strong action on ΔLUMO and ΔHOMO, respectively, are reinforced due to unequal size of MO coefficients in the orbital pairs *s*, -*s* and *a*, -*a*. This is

Table II. Squares of Hückel MO Coefficients for Azulene and Expected Substituent Effects in MCD

	1 = 3	2	4 = 8	5 = 7	6	
- <i>a</i>	0.09	0.00	0.13	0.23	0.00	
- <i>s</i>	0.00	0.10	0.22	0.01	0.26	
	+E	(S)	(D)	(D)	S	D
<i>a</i>	0.29	0.00	0.03	0.11	0.00	
<i>s</i>	0.07	0.34	0.05	0.03	0.13	
	-E	D	S	N	(D)	(S)
position type ^a	sD	dS	dN	Sd	Ds	
contribution to <i>B</i> (L _a)	{ +I	+ -	(+) -	- +	- +	
	{ -I	- +	(-) -	+ -	- +	
	{ +E	(-) (+)	+ -	- +	- +	
	{ -E	- +	~0	(-) (+)	(+) (+)	

^a A lower case letter indicates a weak S or D character and thus weaker response to substituent effects.

due to absence of MO pairing in this nonalternant chromophore and also causes a nonvanishing response to I substitution, unlike that found with alternant even-soft chromophores.^{5,13} Rough pairing of coefficient sizes still remains, however, so that $\text{sgn}(c_{\kappa,1}^2 - c_{\kappa,2}^2) = \text{sgn}(c_{\kappa,2}^2 - c_{-\kappa,1}^2)$, allowing a classification of most positions as +E subdominant, -E dominant (SD, positions 1, 3, 5, and 7) or +E dominant, -E subdominant (DS, positions 2 and 6) with respect to their response to E substitution in the sense of part 3.⁵ The predicted lack of reversal of the substituent effect upon going from a +E to a -E substituent distinguishes the nearly even-soft chromophore **1**, with its positions SD and DS, from polycyclic benzenoid hydrocarbons, which are odd-soft chromophores and whose positions are of types S or D.

Considering alkyls as weak -E substituents, we note that 1,3-disubstitution should indeed make $B(L_a)$ more negative and 6-substitution should make $B(L_a)$ less negative, as observed experimentally. There is little doubt that introduction of much stronger substituents into suitable positions (Table II) will manage to actually reverse the sign of $B(L_a)$ to positive and probably even the sign of $B(L_b)$ to negative. This can be expected for compounds such as 2-OR-**1**, 6-CN-**1**, and 1,3-N-**1**. It would be of interest to test these predictions in order to further evaluate the scope and limitations of the simple theory of part 1-3.³⁻⁵ Such measurements might also help to more closely characterize the detailed nature of substituent action and, conversely, be of value in structure determination.

As in other cyclic π -electron systems, extremely strong -E substitution can be expected⁵ to lead to $B(L_b) > 0$ and $B(L_a) < 0$, as in a parent $(4N + 2)$ -electron annulene, even in a -E subdominant position (DS). This implies a decrease and then a sign reversal for these B terms as the -E substituent effect becomes sufficiently strong, if the substitution is in a position of type DS. Similarly, extremely strong +E substitution should eventually lead to $B(L_b) < 0$ and $B(L_a) > 0$ as in the parent annulene, even in a +E subdominant position (SD), and this in turn implies a decrease and then a sign reversal for these B terms with sufficiently strong +E substituent action if the substitution is in a position of type SD. Whether this limiting behavior can be reached in reality for **1** is not obvious. In part 5,¹³ we noted that it can be reached for pyridine, an alternant even-soft chromophore, but there only the relatively weak resistance put up by the aza nitrogen needed to be overcome by the substituent, while in the present case, the intra-ring cross-link represents a much larger perturbation of the parent perimeter. Still, the preference imposed by such cross-linking can be overcome in the odd-soft chromophore naphthalene.⁸

Conclusions

In MCD spectroscopy, **1** behaves as expected for a molecule intermediate between an even-soft and a positive-hard chromophore. The signs of its L and B bands are in accord with the simple theory of parts 1-3,³⁻⁵ and they, as well as the higher

energy region, are in good agreement with a full PPP calculation using extensive CI. The existence of two new excited states is confirmed; one of these is calculated to be a predominantly doubly excited state.

The signs of B terms of the L bands are insensitive to alkyl substitution as they should be since **1**, strictly speaking, should not be a soft chromophore. Stronger substituents should bring out its approximately even-soft nature, however, and specific recipes have been given for reversing the signs of $B(L_a)$ and $B(L_b)$ by substitution. The observed small effects of alkyls on the magnitude of $B(L_a)$ are in accordance with these arguments.

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References and Notes

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