Electronic Spectra and Electronic Structures of a Series of Bisdehydroannulenes

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Electronic absorption spectra of tetra-*t*-butylbisdehydro[14], [18], [22], [26], and [30]annulenes were investigated experimentally and theoretically. SCF MO calculations were carried out by the P-P-P method and random phase approximation (RPA). An assignment of spectra is presented. Fluorescence excitation polarization spectra of tetra-*t*-butylbisdehydro[14]annulene and the crystalline reflection spectra of tetra-*t*-butylbisdehydro[18]annulene were studied in order to determine the polarization of the spectra. The assignment was confirmed by these methods.

Recently a series of bisdehydroannulenes were synthesized by Nakagawa and coworkers.[1,2] The molecules were shown to have a symmetrical conjugated system. Among interesting physicochemical properties of these molecules, the electronic absorption spectra and fluorescence spectra are of particular interest, since they show a characteristic pattern of conjugated system.

In this paper we will present the assignment of the electronic transitions for bisdehydro[14], [18], [22], [26], and [30]annulenes based on the polarization analyses of the absorption bands with the aid of a crystalline reflectance measurement. The fluorescence polarization technique was also used for determination of the polarization direction. A theoretical calculation of the excited state has been performed, the effect of the bond alternation being examined.

Experimental

The synthesis of the compounds used in this investigation has been described elsewhere.[2] The visisble and UV absorption spectra were measured with a Carl Zeiss spectrophotometer PMQ II, and the fluorescence spectra were recorded with a Carl Zeiss spectrofluorometer. The polarization of the fluorescence was measured with a pola-coat polarizer placed parallel and perpendicular to the fluorescence cell, which was excited by light passed through a calcite polarizer. Reflectivity of a crystal was measured with a reflecting microscope constructed in this laboratory. Calculation of the energy levels of the excited states was carried out by the standard method of Pariser and Parr[3] and Pople[4] with CI calculation and the RPA method developed by Tanaka and Tanaka.[5] All the calculations were performed at Nagoya University Computation Center.

Results and Discussion

Absorption Spectra. The electronic spectra of tetra-*t*-butylbisdehydro[14], [18], [22], [26], and [30]-annulenes were measured in THF solutions in the range 10000—50000 cm^{-1}, four or five allowed transitions being found (Fig. 1). The intensities of these bands are weak, medium, very strong, and strong in the order of increasing energy. Although the location and shape of bands differ for each compound, a common spectral pattern conformable to the spectrum of naphthalene is observed.

We will use the notations used in the classification of polyacene spectra, and call the transitions ^1L_b, ^1L_a, ^1B_b, and ^1B_a bands in the order of increasing energy. A group theoretical classification of the states is also used assuming that the molecule has a D_{2h} symmetry.

Molecular Structure and Theoretical Calculation of Energy Levels. The electronic energy level of a large conjugated system is critically dependent on the precise structure of the molecule. According to the X-ray crystal analysis of Bailey and Mason,[6] and of Kabuto *et al.*[7] the crystals of bisdehydro[14] and [18]annulenes have symmetrical structures, where the center of the molecule is situated in the ceneter of the symmetry of the crystal. Although this does not necessarily indicate a symmetrical structure of the molecule, it is very probable that the molecules have a fully conjugated double bond system. However, according to Kabuto *et al.*[8] bisdehydro[22]annulene shows bond alternation in the crystal which suggests that the larger ring system is stable for the alternate bond structure. A theoretical calculation was carried out for all bisdehydroannulenes assuming that the symmetrical D_{2h} structure has cyclic delocalized double bonds. For bisdehydro[30]annulene, calculation was also carried out with alternate double bond lengths. The results are given in Table 1 together with the observed transition energies and intensities. A comparison of the calculated and observed values gives the following results:

(1) For bisdehydro[14] and [18]annulenes results obtained by the P-P-P and RPA methods are in excellent agreement except that the ^1B_b and ^1B_a transitions are reversed in sequence. The RPA method gives better results with respect to intensity. The ^1B_b and ^1B_a bands are assigned with reference to absorption intensity. The assignment for the ^1B_a band of bisdehydro[18]-annulene is based on the crystalline absorption measurement.

(2) For bisdehydro[22]annulene the agreement is not so good as comapred to small ring molecules. The ^1B_a band is calculated to be low in energy as compared to the observed 33000 cm^{-1} peak. A shoulder around 25000 cm^{-1} region can be assigned to the ^1B_a band.

(3) For bisdehydro[26]annulene the calculated values

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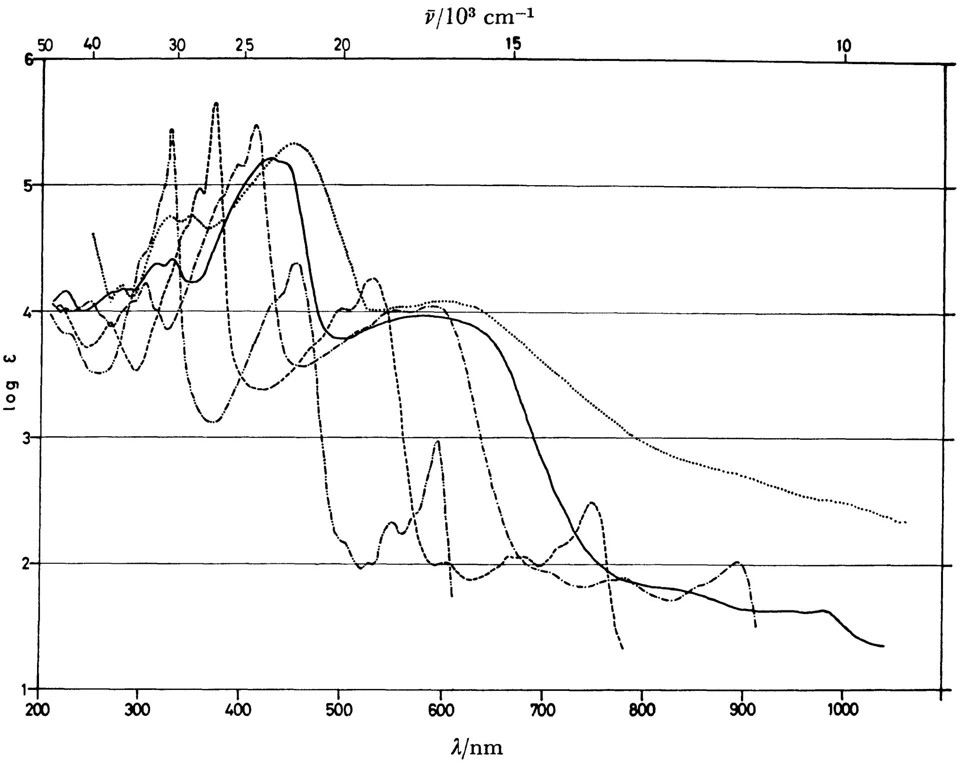

Fig. 1. Electronic absorption spectra of a series of bisdehydroannulenes.
—··—··—: [14], ------: [18], —·—·—: [22], ——: [26], ······: [30]annulene.

TABLE 1. CALCULATED AND OBSERVED ELECTRONIC TRANSITIONS OF BISDEHYDROANNULENES

Number of ring atoms	Calculated transitions				Symmetry	Notation	Observed transitions		
	PPP CI energy (cm^{-1})	f	PPA energy (cm^{-1})	f			Energy (cm^{-1})	f	Polarization
[14]	17040	0	15590	0	B_{2u}	^1L_b	16800	0.003	l
	21530	0.026	21280	0.034	B_{3u}	^1L_a	21980	0.17	s
	33620	2.75	29510	1.39	B_{2u}	^1B_b	30550	1.21	l
	32830	2.62	28670	1.34	B_{3u}	^1B_a	34000	0.20	s
[18]	13270	0	11490	0	B_{2u}	^1L_b	13300	0.001	l
	16820	0.012	16450	0.016	B_{3u}	^1L_a	19000	0.25	s
	29020	4.45	24240	2.08	B_{2u}	^1B_b	26800	1.80	l
	27980	2.53	23760	1.17	B_{3u}	^1B_a	29400	0.20	s
[22]	10910	0	8930	0	B_{2u}	^1L_b	11200	0.004	l
	13840	0.007	13360	0.009	B_{3u}	^1L_a	16600	0.27	s
	26100	6.34	21630	2.79	B_{2u}	^1B_b	24200	2.30	l
	24090	2.32	19920	1.00	B_{3u}	^1B_a	33000	0.23	s
[26]	9310	0	7200	0	B_{2u}	^1L_b	10180	0.0002	l
	11790	0.005	11230	0.006	B_{3u}	^1L_a	15600	0.20	s
	23800	8.23	19420	3.47	B_{2u}	^1B_b	22500	2.20	l
	21240	2.14	17210	0.88	B_{3u}	^1B_a	30200	0.55	s
[30]	(Sym. structure)								
	8170	0	5980	0	B_{2u}	^1L_b			
	10310	0.004	9690	0.004	B_{3u}	^1L_a			
	21930	10.1	17690	4.13	B_{2u}	^1B_b			
	19080	2.0	15200	0.78	B_{3u}	^1B_a			
	(Deform. structure)								
	10860	0	9440	0	B_{2u}	^1L_b	10000	2×10^{-4}	l
	10570	0.002	10290	0.001	B_{3u}	^1L_a	15200	0.21	s
	21240	7.61	18470	3.93	B_{2u}	^1B_b	22200	2.50	l
	18250	1.42	15860	0.73	B_{3u}	^1B_a	28400	0.60	s

are smaller than the observed values. The ^1B_a band is calculated to be too low in energy; it might be buried under the strong band around 24000 cm^{-1} region. If this is the case the 30200 cm^{-1} band should be assigned to another origin.

(4) For bisdehydro[30]annulene the calculated results are also lower in energy than the observed bands; the symmetrical model gives much lower energies than the alternate deformed model. It appears that the molecule has actually an alternate bond structure.

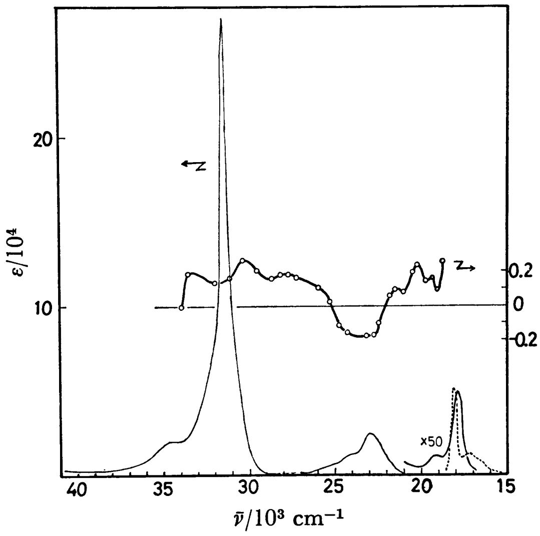

Fig. 2. Electronic absorption (——), fluorescence (······), and fluorescence excitation polarization (APF) spectra (–•–•–) of bisdehydro[14]annulene. p-Values are in the middle of the figure.

Fluorescence Excitation Polarization Spectra. The fluorescence excitation polarization (AFP) of bisdehydro[14]annulene was measured in 2-methyltetrahydrofuran solution at 77 K. The fluorescence was detected at 17100 cm^{-1}. The result is shown in Fig. 2. The fluorescence peak at 77 K was noticeably blue shifted as compared to the absorption peak at room temperature. The polarization of the excitation band defined by $p=I_{//}-I_{\perp}/I_{//}+I_{\perp}$ is also shown. The p-value for the first absorption band is positive (0.25—0.10), while that for the second band (^1L_a band) around 22000 cm^{-1} is negative (−0.19). For the strongest absorption region around 30000 cm^{-1}, the p-value is positive (0.25—0.13), becoming zero at around 33000 cm^{-1}. A theoretical calculation showed the polarization character; the first and the strongest bands are long-axis polarized, the second band is short-axis polarized and another short-axis polarized transition exists at above 30000 cm^{-1}. The result from AFP measurement confirms the theoretical assignment of polarization if we assume that the lowest transition is long-axis polarized. This was confirmed by the crystalline spectra of bisdehydro[18]annulene, and we use this result for bisdehydro[14] and other bisdehydro annulenes. A preliminary result on di-*t*-butyldiphenylbisdehydro[14]-annulene was reported.[1]

Crystalline Spectra of Bisdehydro[18]annulene. In order to find a more reliable assignment of the spectra, the single crystal polarization spectra of bisdehydro[18]-annulene were measured by a reflection method. The solution spectra in 2-methyltetrahydrofuran and the crystalline spectra of bisdehydro[18]annulene are shown in Fig. 3; the crystalline spectra were obtained for the (110) face by the Kramers-Kronig transform of reflectivity. For the first absorption region the absorption was too weak to be measured by means of reflectivity and the transmission measurement was employed.

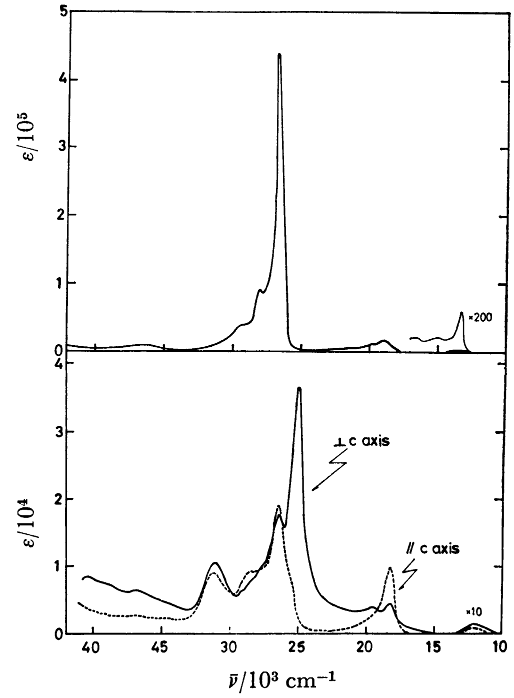

Fig. 3. Solution and the crystalline (110) face spectra of bisdehydro[18]annulene

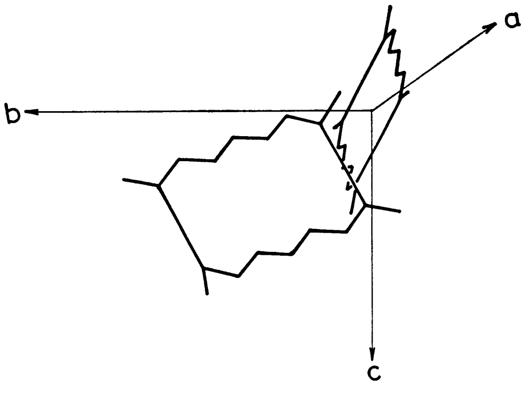

Fig. 4. Projection of molecules onto the (110) face of bisdehydro[18]annulene obtained from Ref. 7.

The projection of molecules onto the developed (110) face is shown in Fig. 4. From the crystalline projection it is easily seen that the short molecular axis of two molecules in a unit cell has a larger component along the c-axis than along the ⊥ c-axis. The long-axis of one of the molecules has a larger component along the ⊥ c-axis on this face, while another molecule has a smaller component. Thus the long-axis polarized transition will appear mainly along the ⊥ c-direction.

The observed spectra clearly show the polarization character of each transition. The first absorption band in the 12000 cm^{-1} region is the weakest one. Such a transition is easily perturbed by the nearby transition. However, the first band shows its own polarization character in which its intensity is stronger along the ⊥ c-axis than along the // c-axis. This means that the first band has long-axis polarization. The second absorption band at 18200 cm^{-1} shows stronger absorption along the // c-axis than along the ⊥ c-axis. Thus it is assigned to the short-axis polarized transition. The third transition, which is the strongest of all transitions, shows peaks at 25000 (0-0), 26400 (0-1) and 27600 (0-2) cm^{-1} along the ⊥ c-axis, and at 26400 (0-0) and 27900—28400 (0-1, 0-2) cm^{-1} along the // c-axis. The splitting of 1400 cm^{-1} for the 0-0 band is due to a Davydov type crystalline splitting. The intensity is stronger along the ⊥ c-axis than along the // c-axis, hence it is assigned to the long-axis polarized band. The fourth absorption band appearing around 31000 cm^{-1} is considered to be the shifted one of 29400 cm^{-1} band in solution. It shows similar strengths of intensity along the ⊥ c and // c directions, and the ⊥ c band may be intensified since the tail of the third band is overlapped with the fourth band. Thus the fourth band is assigned to the short-axis polarized transition. The polarization of transitions was determined from these results (Table 1).

Concluding Remarks

Recently Kolc, Michl, and Vogel[9] studied the electronic spectra of bridged [14]annulenes and calculated excited energies of hypothetical planar [14]annulene. They obtained a similar result similar to ours which shows that the polarization of transitions are along long-, short-, short-, and long-axis in the order of increasing energy. Our theoretical results show a similar tendency, but it is not in harmony with experiment as regard to the third and fourth bands. A reason for this discrepancy may be that the valence state energies of the sp hybridized carbon atoms in the conjugated triple bonds are much larger than those of the sp^2 hybridized carbon atoms; this point was not considered in the present calculation.

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