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The low-lying excited states of 1,6-methano[10]annulene

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Abstract

The electronic absorption spectrum of 1,6-methano[10]annulene in the region of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions was investigated at room and low temperature. By comparison with the one-photon spectrum of naphthalene, and considering pseudoparity selection rules, the strong 33 000 cm^{-1} band of the annulene derivative is assigned as the inductively perturbed $S_0 \rightarrow S_2$ (L_a^+) electronic transition. The rich vibronic structure of the $S_0 \rightarrow S_1$ transition at low temperature is discussed in terms of Franck–Condon allowed transitions. The calculated intensities of the fundamental modes are in qualitative agreement with the experimental data.

Keywords: Electronic absorption spectra; Low-lying excited states; 1,6-Methano[10]annulene

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1. Introduction

Aromaticity is a powerful guideline to the understanding of the properties of conjugated cyclic π-electron systems [1,2]. In the case of annulenes, i.e. the higher homologues of benzene with $(4n+2)$ π electrons, distortion from planarity may decrease the π delocalization and isomerism may occur as a result of the structural flexibility [3]. However, it is generally established [2] that a more rigid σ framework, as supplied by bridgehead links between opposite C atoms or by the formation of triple bonds along the chain, favours the aromatic stabilization of the bond-equalized geometry over the cyclopolyenic arrangement of alternating single and double bonds.

There are good indications that the spectroscopy of bridged [10]-, [14]- and [18]-annulenes conforms to the aromatic behaviour. The subject has been thoroughly discussed in earlier studies [4–6]. In this paper, we address the pseudoparity properties [7] of excited molecular wavefunctions in bridged 1,6-methano[10]annulene (see Fig. 1), due to the nature of alternant hydrocarbon, and the relation with the observed UV spectrum. Pseudoparity selection rules have been used for electronic assignment in simple aromatics [8–10] and may be particularly suitable in the discussion of low-energy transitions of annulenes which remain unclear [6].

Apart from assignment, the excited states of bridged annulenes have not received much attention so far. Their degree of aromaticity or, in other words, to what extent the excitation to virtual molecular orbitals (MOs) changes the cyclic structural arrangement is an important piece of spectroscopic information in its own right as well as in relation to intramolecular photoprocesses. The analysis of the $S_0 \rightarrow S_n$ absorption profiles may provide important clues on this point. If the electronic transition is allowed, the Franck–Condon envelope of vibronic transitions depends, among other things, on the position of the excited state potential well with respect to the ground state [11–13]. To this end, we have measured the $S_0 \rightarrow S_1$ absorption spectrum of 1,6-methano[10]-annulene at low temperature. The intensity profile of the vibronic bands indicates that, on excitation, a geometry change occurs towards a more delocalized structure.

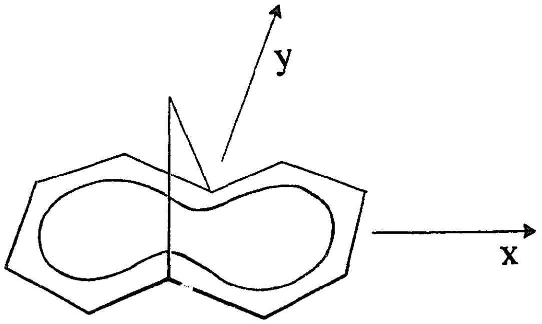

Fig. 1. Molecular structure of 1,6-methano[10]annulene.

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2. Experimental details

1,6-Methano[10]annulene (approximately 1 g) was kindly supplied by Professor Vogel (University of Koln, Koln, Germany). The synthesis of this compound has been described previously [14]. Solutions of 1,6-methano[10]-annulene (10^{-3} M) in isopentane–ether (7:3) were prepared under vacuum in 1 cm quartz cells following thaw–freeze pumping cycles. Spectra were measured at 77 K by means of a closed-circuit, variable-temperature He cryostat with the quartz cell in thermal contact with the cold finger of the cryostat. No loss of optical transparency through the cell was noted during the cooling procedure. The low- and room-temperature spectra of 1,6-methano[10]annulene and naphthalene in cyclohexane were taken on a Cary 5 spectrophotometer.

3. Results and discussion

3.1. Theoretical considerations

The $\pi\pi^*$ one-photon absorption spectrum of catacondensed aromatics (benzene, naphthalene, anthracene, etc.) is usually interpreted in terms of four electronic transitions: L_a, L_b, B_a and B_b in Platt nomenclature [15]. In a first approximation, they are described as being due to one-electron promotion from the two highest occupied MOs (HOMO and HOMO − 1) to the two lowest unoccupied MOs (LUMO and LUMO + 1). According to Huckel theory [1,2], the MO energies are symmetrically displaced around the Coulomb integral α: for one bonding orbital i with energy $\epsilon_i=\alpha+x\beta$ there is a second antibonding orbital i' with energy $\epsilon_{i'}=\alpha-x\beta$, where β is the resonance integral. The pairing property [16] depends on the alternant nature of these systems, i.e. on the possibility of distributing the ring C atoms between two sets such that members of one set are linked only to those of the other set and vice versa. Naphthalene and [10]annulene are alternant hydrocarbons.

Singly excited configurations (SC) $|ij'\rangle$, obtained by promoting one electron from the bonding i to the antibonding j' orbital, are degenerate in alternant systems with $|ji'\rangle$, due to the MO energy ordering [7]. The linear "plus" and "minus" combinations

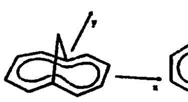
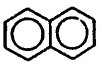
$$ {}^{\pm}V^{ij}=(1/\sqrt{2})(|ij'\rangle\pm|ji'\rangle) \qquad (1)$$

take into rough account the electronic correlation. When the excitation is between MOs i and i', only one configuration $V^{ii}=|ii'\rangle$ is possible. Considering also the ground state configuration V^0, it may be shown [7] that "plus" combinations interact only with "plus" combinations and with V^{ii} excited configurations, while "minus" combinations interact only with "minus" combinations and with V^0. All singly excited configurations are grouped into two classes according to the +; − (or pseudoparity) behaviour. The first comprises ${}^{+}V^{ij}$ and V^{ii} and the second ${}^{-}V^{ij}$ and V^0. Electronic states conserve pseudoparity, being expressed to zero order as combinations of only "plus" (or "minus") configurations.

Although pseudoparity is strictly related to the Huckel (or, at most, the Pariser–Parr–Pople (PPP)) model, it remains approximately valid in semiempirical MO/SCI calculations. Thus the lowest excited states of naphthalene are mostly described as $\mathrm{L}_b^-\approx(|\mathrm{HOMO},\ \mathrm{LUMO}+1\rangle-|\mathrm{HOMO}-1,\ \mathrm{LUMO}\rangle)$, $\mathrm{L}_a^+\approx|\mathrm{HOMO},\ \mathrm{LUMO}\rangle$, $\mathrm{B}_b^+\approx(|\mathrm{HOMO},\ \mathrm{LUMO}+1\rangle+|\mathrm{HOMO}-1,\ \mathrm{LUMO}\rangle)$, $\mathrm{B}_a^+\approx|\mathrm{HOMO}-1,\ \mathrm{LUMO}+1\rangle$, denoting by a and b the polarization directions of the corresponding state along the short and long molecular in-plane axes respectively. Results of calculations on naphthalene within the INDO/SCI approximation and using the whole $\pi\pi^*$ configuration space are shown in Table 1. The calculation was repeated with 1,6-methano[10]annulene, using the equilibrium geometry optimized, as in the previous case, by means of ab initio methods (see Table 1). The excitation energies increase with increasing 1,6 transannular interaction, i.e. from 1,6-methano[10]annulene to naphthalene, in agreement with early estimates [6]. Excited $\pi\pi^*$ states of 1,6-methano[10]annulene conserve the naphthalene pseudoparity, with three (L_a^+, B_b^+, B_a^+) of "plus" character and one (L_b^-) of "minus" character. From this point of view, the present result suggests that 1,6-methano[10]annulene should be considered as a perturbed naphthalene system. This conclusion is also supported by the close similarity of the energy ordering and coefficients of the MOs among which the electrons are promoted to give the abovementioned $\pi\pi^*$ states. For correlation purposes, it is interesting to consider also the excited $\pi\pi^*$ states of the hypothetical planar [10]annulene molecule. This procedure has been adopted in this [6] and a similar [5] case, assuming regular polygon geometries. The four electronic transitions of planar [10]annulene are classified, according to INDO/SCI calcu-

Table 1

The lowest one-photon active transitions of the hypothetical planar [10]annulene, 1,6-methano[10]annulene and naphthalene; INDO/SCI results of excitation energies (cm^{-1}) and oscillator strengths (upper and lower entries for each state). The calculation includes the full $\pi\pi^*$ orbital space. The molecular geometries have been optimized using the GAMESS program [17] and the 6-31G basis set with D_{2h} symmetry for [10]annulene and naphthalene and C_{2v} symmetry for 1,6-methano[10]annulene

State			
L_b^-	22590	28460	32810
	0.027	0.0036	0.0026
L_a^+	30670	33520	37840
	0.011	0.091	0.153
B_b^+	42580	40760	45943
	2.470	1.391	1.830
B_a^+ (B_a^-) [a]	40170	45030	49020
	1.555	0.560	0.660

[a] The pseudoparity symmetry of planar [10]annulene is given in parentheses.

lations on the optimized structure kept planar at D_{2h} symmetry, as L_b^-, L_a^+, B_b^+, B_a^- (see Table 1). The change in the number of states of equal pseudoparity may be justified recalling that, according to Huckel theory, the [10]annulene ring has two degenerate HOMOs and two degenerate LUMOs. Both split into pairs when the symmetry is D_{2h} with energy gaps HOMO−1/HOMO and LUMO+1/LUMO sufficiently small to have "plus" and "minus" combinations of |HOMO, LUMO⟩ and |HOMO−1, LUMO+1⟩ configurations. The two energy gaps increase considerably in 1,6-methano[10]annulene and naphthalene reducing the configuration mixing and, in the limit of the approximation of the pseudoparity theory, three "plus" and one "minus" states occur.

3.2. The electronic assignment

The one-photon spectrum of 1,6-methano[10]annulene (1.5×10^{-4} M) in cyclohexane is shown in Fig. 2 (trace a). For comparison, the spectrum of equimolar naphthalene is also reported (trace b), with the well-known first (L_b^-, weak) and second (L_a^+, moderately strong) electronic transitions. The experimental intensity ratio between the two naphthalene transitions is approximately 80 in favour of the latter, in good agreement with reported intensity values [18]. Here, on the basis of pseudoparity symmetry, the correlation of the two lowest absorption systems of 1,6-methano[10]annulene to the L_b^- and L_a^+ transitions of naphthalene is suggested. This correspondence has been proposed previously for the lowest transition [4–6]. More uncertainty exists on the assignment of the second absorption band [6].

Considering the spectral data of Fig. 2 on the annulene derivative, it is found that the first absorption system, $S_0\rightarrow S_1$, becomes stronger by a factor of approximately 1.5, while the second becomes weaker by a factor of approximately 0.75, with respect to the corresponding bands of naphthalene. Since one-photon processes couple states of different pseudoparity, $-\rightarrow+$ and vice versa, and the ground state has "minus" symmetry [7], the L_b^- transition is pseudoparity forbidden while L_a^+ is pseudoparity allowed. In first order, however, "plus" and "minus" states may interact if the molecular hamiltonian is perturbed and, as a consequence, the pseudoparity selection rules may relax. There are two common sources of perturbations: one due to substituents (or inductive), influencing the Coulomb integral α, and the second vibronic, related to the hamiltonian dependence on the normal coordinates, affecting the resonance integral β [8]. In the first case, i.e. inductive perturbation, states of different pseudoparity are mixed, whereas in the other, mixing conserves pseudoparity [8]. Due to this, it is expected that the inductive effect, coupling "minus" with "plus" states, strengthens L_b^-, with intensity borrowing from the upper L_a^+ state. In contrast, the L_a^+ transition intensity will be depressed due to the same effect. The qualitatively good correspondence with experimental intensity data, as given previously, supports the assignment of the broad band around 33 000 cm^{-1} of 1,6-methano[10]annulene to the inductively perturbed L_a^+ transition. Incidentally, we note that, on going from naphthalene to 1,6-methano[10]annulene, the calculated oscillator strengths ($f(L_a^+)$, $f(B_b^+)$ and $f(B_a^+)$) decrease, whereas $f(L_b^-)$ increases, in agreement with experiment. In contrast, a more irregular behaviour is observed when the comparison is made with calculated f values of planar [10]annulene.

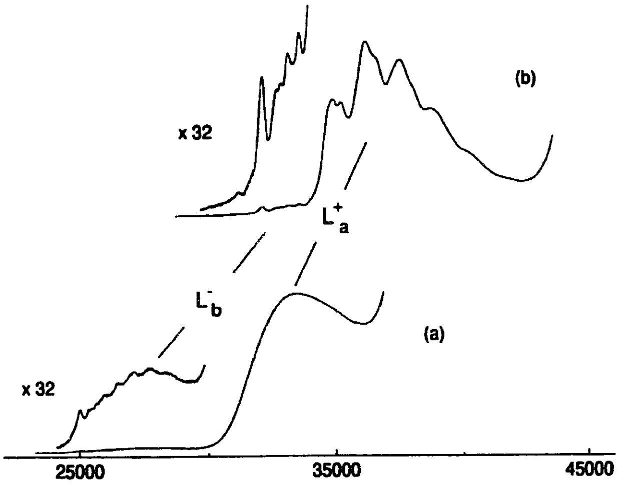


Fig. 2. Room-temperature absorption spectra of 1,6-methano[10]annulene (a) and naphthalene (b) ($c=1.5\times10^{-4}$ M in cyclohexane) in the region of the two lowest electronic transitions, L_b^- and L_a^+.

3.3. The low-temperature $S_0\rightarrow S_1$ absorption spectrum

The vibronic structure of the $S_0\rightarrow S_1$ (L_b^-) transition is well resolved for a glassy matrix of 1,6-methano[10]-annulene at 77 K. The spectrum is shown in Fig. 3. The electronic origin, observed at 25 084 cm^{-1}, has a gaussian profile, due to the random orientation of solute molecules inside the matrix, with an inhomogeneous bandwidth of

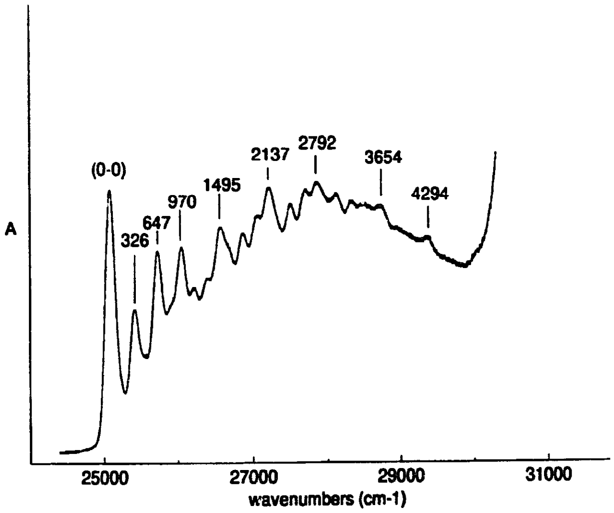


Fig. 3. $S_0\rightarrow S_1$ absorption spectrum of 1,6-methano[10]annulene (10^{-3} M) in isopentane–ether at 77 K. The electronic origin (0–0) is observed at 25 084 cm^{-1}. The main vibrational intervals (cm^{-1}) from (0–0) are also indicated in the figure.

approximately 190 cm^{-1} (full width at half-maximum (FWHM)). The strongest vibronic bands are found at 326, 647, 970, 1495, 2137 and 2792 cm^{-1} from (0–0). Several others have appreciable intensity, being more diffuse with increasing energy. The vibronic frequencies are reported in Table 2.

It has already been established through polarization degree measurements on the excitation spectrum [6] that the L_b^- origin, as well as the vibronic additions, has a long-axis (x) polarization direction. The vibronic structure may therefore be discussed in terms of Franck–Condon allowed transitions. To this end, we recall [11–13] that the intensity of the $S_{0,0} \rightarrow S_{1,\upsilon}$ vibronic transition is determined by the Franck–Condon factor $|\langle 0_g | \upsilon_e \rangle|^2$, where $|0_g\rangle$ and $|\upsilon_e\rangle$ are the vibrational wavefunctions of a given normal mode in the ground (g) and excited (e) states. Assuming no change in harmonic frequency in the two states, the Franck–Condon factors are expressed in closed form as [11]

$$|\langle 0_g | \upsilon_e \rangle|^2 = e^{-\gamma} \gamma^{\upsilon} / \upsilon! \qquad (2)$$

where the adimensional parameter γ depends on the ground and excited state equilibrium geometries and on the normal mode cartesian displacements [12,13]. It is unlikely that the three lowest vibronic transitions (326, 647 and 970 cm^{-1}), although approximately equally spaced, form a vibrational progression on the first mode. In fact, given the large intensity difference between the (0–0) and 326 cm^{-1} bands, possible overtone transitions should have, in view of Eq. (2), vanishing strength for $\upsilon = 2$. Reasonably, most of the vibronic transitions up to approximately 1600 cm^{-1} from (0–0) are due to excited state fundamentals. As previously noted, above this limit, bands are increasingly diffuse and a reliable assignment becomes more difficult. Tentatively, vibrational progressions of the 647 cm^{-1} mode built on the other totally symmetric modes may be identified. Our proposed assignment is reported in Table 2.

Table 2
The $S_0 \rightarrow S_1$ absorption spectrum of 1,6-methano[10]annulene at 77 K; observed absolute frequencies (ω, cm^{-1}), relative intensities (I), differences Δ (cm^{-1}) with respect to (0–0) and proposed assignment. The letters a–h denote the excited state totally symmetric fundamentals

ω	I [a]	Δ	Assignment [b]	
25084	s	–	(0–0)	
25410	m	326	a	
25731	ms	647	b	
25914	sh	830	c	
26054	m	970	d; (a+b)?	
26228	w	1144	e	
26393	w	1309	f; 2b?	
26579	m	1495	g	
26680	sh	1596	h; (b+d)?	
26876	w	1792	e+b	(1)
27055	w	1971	f+b	(15)
27221	mw	2137	g+b	(−5)
27511	w	2427	(e+2b)?; (g+d)?	
27700	w	2616	f+2b	(13)
27876	mw	2792	g+2b	(3)
28132	w	3048	(e+3b)?	(−37)
28338	w	3254	f+3b	(4)
28512	w	3428	g+3b	(−8)
28738	w	3654	2g+b	(17)
28970	w	3886	?	
29378	w	4294	2g+2b	(10)

[a] s, strong; m, medium; w, weak; sh, shoulder.

[b] The (0–0) frequency is implicitly taken into account in the assignment of all vibronic lines. The difference between the observed and calculated combination frequencies is given in parentheses.

Table 3
Strongest totally symmetric vibronic fundamentals of the $S_0 \rightarrow S_1$ transition, as determined by the QCFF/PI semiempirical calculation; ω, fundamental frequency (cm^{-1}); $I_{1\upsilon}/I_{00}$, vibronic intensity with respect to that of the electronic origin (see Eq. (2)). The only modes considered are those for which $I_{1\upsilon}/I_{00} > 0.1$

ω	$I_{1\upsilon}/I_{00}$
1486	0.451
1430	0.195
1022	0.115
964	0.150
413	0.825
378	0.380

Finally, the Franck–Condon factors and intensities of the totally symmetric fundamentals have been evaluated on the basis of semiempirical QCFF/PI MO calculations [19], a procedure that has given good theoretical results in other instances [12,13,20,21]. The vibronic intensities with respect to that of the (0–0) transition, $I_{1\upsilon}/I_{00}$, have been calculated following the S_0 and S_1 geometry optimization within the QCFF/PI approximation. In Table 3, we only report the results for the totally symmetric ground state modes with intensity ratios larger than 0.1. On the whole, a qualitative agreement with the experimental results is found. All vibronic transitions are predicted to be weaker than the electronic origin and with Franck–Condon activity mostly centred on the two low-frequency modes and on the C–C stretching vibration calculated at 1486 cm^{-1}. Our preliminary indication on S_1, resulting from these calculations, is that a structural change occurs on excitation to S_1 towards a C_{2v} geometry with more balanced C–C bond lengths. Additional excited state minima, similar to those of the ground state [22], may be determined with the help of more powerful ab initio methods.

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