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The Electronic Structures and Spectra of Benzocyclobutenes and of Biphenylene Derivatives

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Abstract: The UV–vis spectra of the benzocyclobutenes **1–6**, of the dications and dianions of **1** and **2**, and of the biphenylene derivatives **7** as well as of the phenanthrocyclobutenes **8** have been studied by means of PPP calculations. The agreement between experimental and theoretical transition energies and moments for the few known compounds is very good, so that our predictions for the yet unknown compounds are reliable. For the benzocyclobutenes **2** we obtain in agreement with experiment a hypsochromic shift of the lowest transition with increasing number of annelated benzene rings. This is in contrast to the bathochromic shift of the acene series. For the benzobicyclobutenes **4** we also obtain a hypsochromic shift whereas the series **6** and the dications and dianions of **2** show a bathochromic shift with increasing number of benzene rings. The calculated properties of 1,2-diphenylphenanthro[1]cyclobutene (**8b**) and of the isomeric nonalternant hydrocarbons **9** are different from the properties of a compound synthesized by Bergmann and Agranat[1] to which they ascribed the formula **8b**. We suggest for this compound the structure of the butatriene **12**.

For compounds **1–8** many calculations of ground state properties are to be found in the literature[2-8] but according to our knowledge the UV–vis spectra of such compounds have not yet been treated with more sophisticated methods than the Hückel scheme.[5] We have calculated singlet transition energies and moments using the PPP method[9] with the parametrization of Pancir, Matoušek, and Zahradník.[10] Compared to standard treatments and parametrizations, this method, which utilizes a single set of parameters based on atomic spectral data, gave a better agreement between theory and experiment, including both ground-state properties and electronic spectra for a number of conjugated compounds.[10] Since we are dealing with pure hydrocarbons we use the all-β (AB) approximation.[10] The excited states have been obtained by a limited configuration interaction between 50 configurations, which are the lowest excited singlet configurations selected lexicographically. We shall restrict our discussion to the lowest transitions, because we did not take into consideration doubly excited configurations which are important for the higher excited states. The theoretical extinction coefficients ϵ are obtained from the calculated oscillator strengths f using the relationship[10,11] $\log \epsilon = \log f + 4.5$. The geometry was determined in an iterative manner from the calculated bond orders ("SC procedure"). The starting geometry consists of regular polygons with all bond lengths equal to 1.397 Å and exo bonds bisecting the bond angle. Only resonance integrals and electron repulsion integrals between neighbors were adjusted in this procedure. Compounds with phenyl ligands have been studied with distortion angles $\varphi = 0$ and 90° between the plane of the phenyl group and the plane of the rest of the molecule. The results for $\varphi = 90°$ do not differ significantly from those for the corresponding hydrocarbons without phenyl ligands. Therefore, we only discuss our results for $\varphi = 0°$.

All the calculated transition energies and extinction coefficients together with the experimental values are given in Table I.

Results

Benzocyclobutenes 1–6. The compounds **1c** and **1d** have not yet been synthesized. **1a** and **1b** have been detected as reactive intermediates.[12,13] Calculations on the ground-state stability show that only **1c** might be isolable.[8] On the contrary the synthesis of **2b**[14] and **2c**[15] has been reported as well as that of the tetramethyl derivative **2a'**.[16] Some portion of the stability of **2a–2c** must be related to the steric hindrance to dimerization offered by the phenyl groups.[8] Perhaps the introduction of other bulky groups might allow the isolation of **1a** and **1b**. The distortion angle φ of the phenyl groups in **2a–c** is not known. The calculated longest wavelength absorption in **2b** and **2c** differs from the experimental values less than 0.1 eV. Also the difference between theoretical and experimental extinction coefficients is satisfactory. In **2a–c** a distortion angle $\varphi = 90°$ would shift the lowest transition about 0.5 eV to higher energies (cf. **1a–c**) and the extinction coefficients would be considerably reduced. Therefore, one can suppose that in **2b** and **2c** the phenyl groups are in conjugation with the rest of the molecule. The phenyl groups in **2a'** are certainly a little distorted, since the experimental transition energy is about the mean value of **2a** ($\varphi = 0°$) and **1a**. The experimental extinction coefficient of **2a'** is also smaller than the calculated one of **2a**. The experimental value of the lowest transition in **2b'** (3.10 eV, log $\epsilon = 3.7$)[17] is shifted by 0.38 eV to higher energy compared to that of **2b**. In a test calculation of **2b'** the two phenyl groups and the two carboxy groups on the benzene ring reduce the calculated lowest transition energy of **2b** less than 0.05 eV. In **1b** the lowest transition energy is nearly unchanged only if either the two phenyl groups or the two carboxy groups are added to the benzene ring. Altogether they would reduce the transition energy of **1b** by 0.27 eV. Therefore, we can conclude that in **2b'** all four phenyl groups are highly distorted. With the increasing number of benzene rings in **2** the calculated and experimental lowest transition is shifted to higher energies as opposed to the acene series which shows a bathochromic shift.[18]

Table I. Calculated and Observed Transition Energies S (eV) and Extinction Coefficients log ϵ of the Lower Excited Singlet States of **1-11** and of the Dications and Dianions of **1** and **2**

Compd	S (calcd)	Log ϵ (calcd)	Predominant configuration (%)	S (obsd)	Log ϵ (obsd)	Ref
1a (C_{2v})	2.93	0.84	$4 \rightarrow 5$ (98) B_1			a
	3.94	2.99	$4 \rightarrow 6$ (64) A_1			
			$3 \rightarrow 5$ (34)			
1b (C_{2v})	3.13	2.05	$6 \rightarrow 7$ (97) B_1			
	3.53	2.23	$6 \rightarrow 8$ (49) A_1			
			$5 \rightarrow 7$ (43)			
1c (C_{2v})	3.20	0.55	$8 \rightarrow 10$ (45) A_1			
			$7 \rightarrow 9$ (41)			
	3.28	2.59	$7 \rightarrow 10$ (95) B_1			
1d (C_{2v})	3.01	2.32	$10 \rightarrow 12$ (45) A_1			
			$9 \rightarrow 11$ (36)			
	3.18	3.86	$10 \rightarrow 11$ (94) B_1			
1a^{2+} (C_{2v})	2.81	2.72	$3 \rightarrow 4$ (98) B_1			
	3.88	2.78	$3 \rightarrow 5$ (72) A_1			
1b^{2+} (C_{2v})	1.34	2.59	$5 \rightarrow 6$ (98) B_1			
	2.68	3.03	$5 \rightarrow 7$ (66) A_1			
1c^{2+} (C_{2v})	0.57	2.24	$7 \rightarrow 8$ (96) B_1			
	2.03	3.48	$7 \rightarrow 9$ (62) A_1			
1a^{2-} (C_{2v})	2.39	2.21	$5 \rightarrow 7$ (97) B_1			
	2.83	3.09	$5 \rightarrow 6$ (65) A_1			
			$4 \rightarrow 7$ (35)			
1b^{2-} (C_{2v})	1.43	2.06	$7 \rightarrow 8$ (95) B_1			
	2.22	2.00	$7 \rightarrow 9$ (57) A_1			
			$6 \rightarrow 8$ (41)			
1c^{2-} (C_{2v})	0.89	1.78	$9 \rightarrow 10$ (91) B_1			
	1.90	2.92	$8 \rightarrow 10$ (49) A_1			
			$9 \rightarrow 11$ (45)			
2a (C_{2v})	2.42	3.68	$10 \rightarrow 11$ (92) B_1	2.65	3.25	b
	3.70	3.66	$10 \rightarrow 13$ (40) A_1			
2b (C_{2v})	2.66	3.82	$12 \rightarrow 13$ (95) B_1	2.72	3.71	14
	3.39	3.19	$12 \rightarrow 14$ (54) A_1			
			$11 \rightarrow 13$ (30)			
2c (C_{2v})	2.78	3.95	$14 \rightarrow 15$ (95) B_1	2.82	3.68	15
	3.12	2.51	$14 \rightarrow 16$ (44) A_1			
			$13 \rightarrow 15$ (37)			
2d (C_{2v})	2.90	4.08	$15 \rightarrow 17$ (98) B_1			
	2.97	1.31	$16 \rightarrow 17$ (39) A_1			
			$15 \rightarrow 18$ (38)			
2a^{2+} (C_{2v})	2.70	−0.64	$8 \rightarrow 10$ (89) B_1			
	2.80	4.73	$7 \rightarrow 10$ (80) B_1			
2b^{2+} (C_{2v})	1.56	2.19	$11 \rightarrow 12$ (96) B_1			
	2.60	3.80	$10 \rightarrow 12$ (65) A_1			
			$11 \rightarrow 13$ (31)			
2c^{2+} (C_{2v})	0.77	0.17	$13 \rightarrow 14$ (96) B_1			
	2.14	2.95	$13 \rightarrow 15$ (65) A_1			
			$12 \rightarrow 14$ (30)			
2a^{2-} (C_{2v})	1.94	3.60	$11 \rightarrow 13$ (68) B_1			
	2.05	3.68	$11 \rightarrow 14$ (69) B_1			
2b^{2-} (C_{2v})	1.35	3.27	$13 \rightarrow 14$ (95) B_1			
	1.97	3.96	$13 \rightarrow 15$ (83) A_1			
2c^{2-} (C_{2v})	0.87	2.80	$15 \rightarrow 16$ (94) B_1			
	1.83	3.47	$15 \rightarrow 17$ (70) A_1			
3a (D_{2h})	1.36	2.13	$5 \rightarrow 6$ (99) B_{2u}			
	1.70	3.15	$5 \rightarrow 7$ (65) B_{3u}			
			$4 \rightarrow 6$ (34)			
3b (D_{2h})	2.56	0.89	$7 \rightarrow 8$ (94) B_{2u}			
	3.28	3.00	$7 \rightarrow 10$ (58) B_{3u}			
			$6 \rightarrow 8$ (37)			
3c (D_{2h})	2.96	2.35	$9 \rightarrow 10$ (87) B_{2u}			
	3.06	2.40	$9 \rightarrow 11$ (49) B_{3u}			
			$8 \rightarrow 10$ (43)			
3d (D_{2h})	2.93	1.14	$11 \rightarrow 13$ (46) B_{3u}			
			$10 \rightarrow 12$ (43)			
	3.23	3.36	$10 \rightarrow 13$ (76) B_{2u}			
4a (D_{2h})	1.08	2.82	$17 \rightarrow 18$ (100) B_{2u}	1.93		c
	1.48	3.54	$17 \rightarrow 19$ (70) B_{3u}			
4b (D_{2h})	2.22	3.78	$19 \rightarrow 20$ (89) B_{2u}			
	2.75	$-\infty$	$19 \rightarrow 21$ (77) B_{1g}			
4c (D_{2h})	2.58	4.09	$21 \rightarrow 22$ (82) B_{2u}			
	2.86	$-\infty$	$21 \rightarrow 23$ (66) B_{1g}			
4d (D_{2h})	2.78	4.29	$23 \rightarrow 24$ (73) B_{2u}			
	2.89	2.86	$23 \rightarrow 26$ (46) B_{3u}			
			$22 \rightarrow 24$ (38)			

Table I *(Continued)*

Compd	S (calcd)	Log ϵ (calcd)	Predominant configuration (%)	S (obsd)	Log ϵ (obsd)	Ref
5a (C_{2v})	3.07	2.42	$5 \to 7$ (94) A_1			
	3.20	2.41	$4 \to 6$ (96) A_1			
5b (C_s)	2.58	2.34	$7 \to 8$ (85) A''			
	3.02	2.34	$7 \to 9$ (50) A''			
			$6 \to 8$ (32)			
5c (C_s)	2.34	3.00	$9 \to 10$ (82) A''			
	2.91	2.72	$9 \to 11$ (45) A''			
			$8 \to 10$ (30)			
5d (C_s)	2.17	3.34	$11 \to 12$ (73) A''			
	2.84	3.01	$11 \to 13$ (42) A''			
			$10 \to 12$ (25)			
6a (C_{2v})	2.62	2.88	$17 \to 18$ (77) B_1			
	2.76	4.11	$17 \to 19$ (68) A_1			
	2.83	2.69	$16 \to 18$ (64) A_1			
			$17 \to 19$ (29)			
6b (C_s)	2.24	3.36	$19 \to 20$ (88) A''			
	2.80	3.86	$18 \to 21$ (63) A''			
			$19 \to 21$ (21)			
	2.88	3.38	$18 \to 20$ (38) A''			
			$19 \to 21$ (34)			
6c (C_s)	2.00	3.06	$21 \to 22$ (95) A''			
	2.83	2.90	$21 \to 23$ (44) A''			
	2.89	4.05	$20 \to 23$ (82) A''			
6d (C_s)	1.88	2.94	$23 \to 24$ (88) A''			
	2.78	3.23	$23 \to 26$ (32) A''			
			$23 \to 25$ (25)			
	2.93	4.01	$22 \to 25$ (94) A''			
7a (D_{2h})	3.24	$-\infty$	$6 \to 7$ (97) B_{1g}	3.15	Weak	34
	3.72	3.63	$6 \to 8$ (71) B_{3u}	3.50	3–4	
7b (C_{2v})	2.37	0.79	$8 \to 9$ (99) B_1	2.00	1.63	21, 22
				2.22	2.42	
				2.42	2.69	
				2.59	2.81	
	2.97	1.62	$8 \to 10$ (80) B_1	2.68	3.00	
7c (D_{2h})	2.05	$-\infty$	$10 \to 11$ (95) B_{1g}			
	2.30	2.34	$9 \to 11$ (93) B_{3u}			
7d (C_{2v})	2.81	2.91	$9 \to 10$ (94) B_1			
	3.16	1.63	$9 \to 11$ (92) B_1			
7e (C_{2v})	2.80	2.75	$14 \to 17$ (95) B_1			
	3.01	2.60	$15 \to 17$ (48) A_1			
			$14 \to 16$ (43)			
7f (C_{2v})	2.29	0.96	$11 \to 12$ (83) B_1			
	2.61	2.84	$10 \to 12$ (75)			
7g (C_{2v})	2.29	0.74	$17 \to 18$ (80) B_1			
	2.64	2.33	$15 \to 18$ (82) B_1			
7h (D_{2h})	2.74	$-\infty$	$12 \to 13$ (73) B_{1g}			
	2.80	3.01	$11 \to 13$ (91) B_{3u}			
7i (D_{2h})	2.70	$-\infty$	$23 \to 25$ (77) B_{1g}			
	2.85	2.11	$22 \to 25$ (93) B_{3u}			
	2.88	3.88	$24 \to 25$ (61) B_{2u}			
			$23 \to 26$ (27)			
8a (C_{2v})	2.24	3.20	$8 \to 9$ (91) B_1			
	3.11	3.11	$8 \to 10$ (63) A_1			
			$7 \to 9$ (27)			
8b (C_{2v})	1.89	2.55	$14 \to 15$ (99) B_1			d
	3.11	3.48	$14 \to 17$ (73) A_1			
8c (D_{2h})	2.05	$-\infty$	$14 \to 15$ (98) B_{1g}			
	3.07	3.76	$14 \to 16$ (76) B_{3u}			
9a (C_{2v})	2.66	3.90	$14 \to 15$ (98) B_1	2.84	3.60	29
	3.35	4.42	$14 \to 16$ (96) A_1	3.30	4.50	
9b (C_s)	3.33	3.69	$14 \to 15$ (57) A''			
			$12 \to 15$ (20) A''			
	3.55	3.83	$13 \to 15$ (43) A''			
			$14 \to 15$ (23)			
9c (C_s)	1.63	2.82	$14 \to 15$ (97) A''			
	2.58	3.07	$14 \to 16$ (84) A''			
10 (C_s)	3.38	2.91	$8 \to 10$ (94) A''	3.41	4.56	35
	3.60	4.19	$8 \to 9$ (79) A''			
X = 12^d				2.68	4.02	1, 31
				4.13	3.95	

^{a} The reported UV spectrum of **1a** matrix isolated in argon[12] seems to be unreliable to determine the longest wavelength absorption. ^{b} Values of **2a'**.[16] ^{c} Value of **4a'**; the correct molecular coefficient in the UV spectrum could not be obtained.[19] ^{d} Cf. phenanthrocyclobutene section.

ta   tb   lc   td

6b   6c   6d

2a   2a'   2b   2b'

2c   2d   3a   3b

7a   7b   7c   7d   7e

3c   3d   4a   4a'

7f   7g   7h   7i   8a

4b   4c   4d   5a

8b   8c   9a   9b   9c

5b   5c   5d   6a

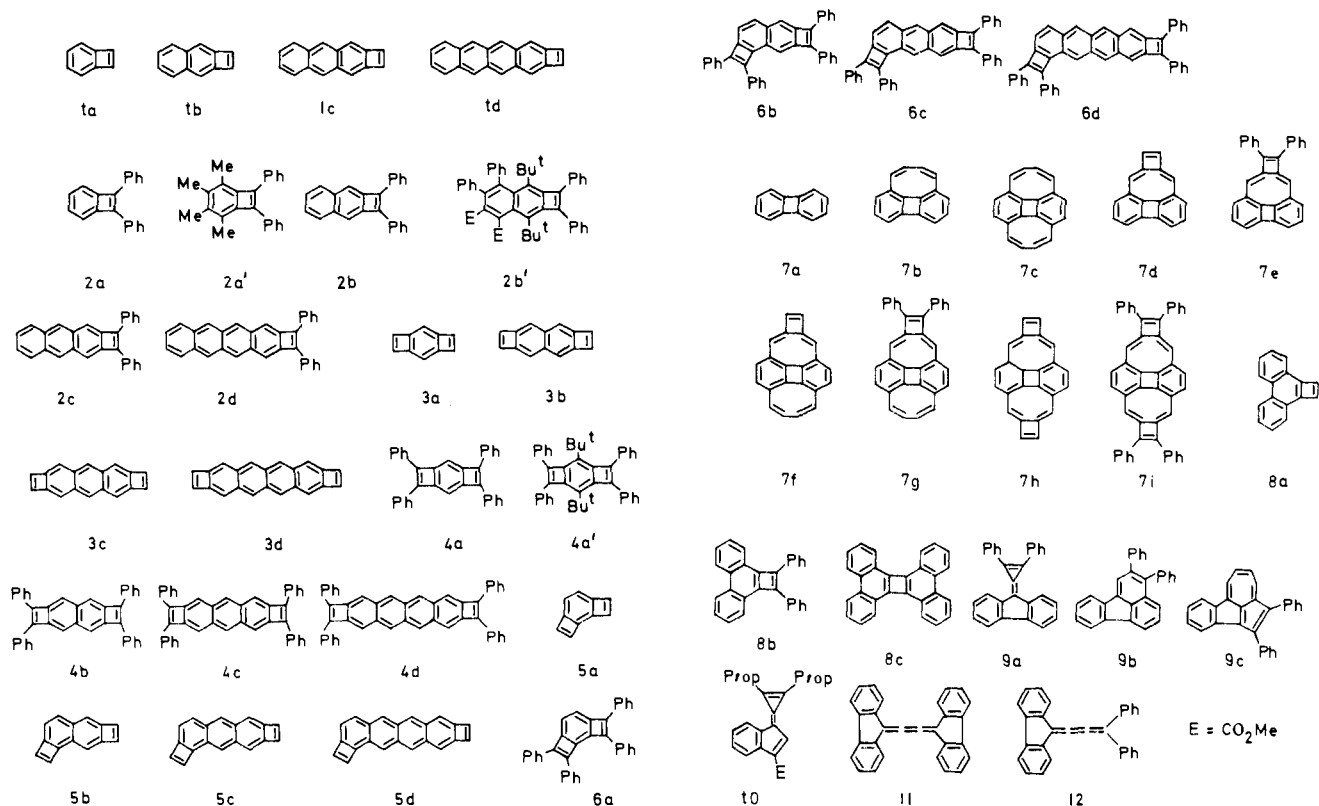Prop   Prop   E = CO$_2$Me

to   ll   l2

Figure 1. Compounds under study.

The corresponding compounds without phenyl substituents **1a–c** show the same behavior, whereas **1d** has again almost the same transition energy as **1a**. The reason for this is that in **2a–d** the state with symmetry B$_1$ remains the lowest excited singlet state, whereas in **1a–d** there is a crossing between the states with symmetry A$_1$ and B$_1$.

Only the derivative **4a'** of **4a** of the polyacenes with two annelated cyclobutenes is known as a fairly stable compound.[19] A graph theoretical investigation[7] predicts for **3a** very low chemical stability in contrast to **5a**. The stability of **4a'** can certainly be attributed to the effect of the phenyl and *tert*-butyl groups. The experimental lowest transition energy of **4a'** is, however, about 0.57 eV higher than the calculated one for **3a**. We have chosen **3a** for comparison, since one can expect that in **4a'** the phenyl groups are distorted as in **2b'**. The energy of the lowest doubly excited configuration (doubly excitation HOMO–LUMO) in **1a–d**, **2a–d**, **3b–d**, and **4b–d** is considerably higher than that of our calculated lowest excited singlet state. This doubly excited configuration would contribute to the ground state of these compounds less than 2.8% and can therefore be neglected. However, in **3a** and **4a** the contribution of this doubly excited configuration would be more than 10% and the energy of the ground state would be lowered by more than 0.17 eV. The importance of doubly excited configurations in **3a** or **4a** is not surprising, since HMO theory would lead to an open shell structure for **3a**.[7] Furthermore the energy difference between the lowest excited singlet state of **3a** and **4a** given in Table I and the lowest doubly excited configuration is less than 0.17 eV. Therefore, it is impossible to reproduce the experimental value of **4a'** without extensive use of doubly excited configurations. The course of the calculated lowest transition energies of **3** and **4** is similar to that of **1** and **2**. Extrapolation from **3c** and **3d** yields about the experimental value of **4a'**.

Although **5a** should be more stable than **3a**[7] a member of **5** or **6** has not yet been synthesized. Doubly excited configurations have not been considered as in **3a** or **4a**. It is interesting

that in **5** or **6** the lowest transition energy decreases with the increasing number of benzene rings as in the acene series[18] and in contrast to **1–4**.

The dication of a dimethyl derivative of **1a** has been recently synthesized but unfortunately no UV–vis spectrum was given.[20] The longest wavelength absorption of the dications and dianions of **1** and **2** shows an extreme bathochromic shift with increasing annelation. This is smaller for the dianions than for the dications as well as for the compounds with phenyl groups (**2**$^{2+}$ or **2**$^{2-}$) compared to those without phenyl groups (**1**$^{2+}$ or **1**$^{2-}$). These lowest transitions are almost pure HOMO–LUMO excitations. The decreasing orbital energy differences between the HOMO and the LUMO with increasing number of annelated benzene rings leads to this bathochromic shift. It should be noted that it is impossible to obtain reliable results for the dications and dianions of **3–6** without the inclusion of doubly excited configurations.

Biphenylene Derivatives 7. Only the parent compounds **7a** and **7b**[21,22] are known of the biphenylene derivatives **7**.[23] The theoretical lowest transition energy of **7a** differs from the experimental value less than 0.1 eV and is forbidden by symmetry. The long wavelength band of **7b** shows a distinct vibrational structure.[22] Here the first and the second excited singlet state are calculated about 0.3 eV at too high an energy. Perhaps our chosen parametrization is not optimal for compounds like **7b** containing polyene structures with a strong bond length alternation. It might be that here the interaction with σ → σ* configurations will lower the first excited singlet state as was shown in the case of butadiene.[24] Wilcox and co-workers[22] found that this long wavelength band is a nearly forbidden out-of-phase combination[25] of the long-wavelength bands of **7a** and of *cis*-butadiene. This is fully confirmed by our calculations as follows. The lowest transition of **7b** consists of more than 96% of the HOMO–LUMO excitation. The same is true for **7a** and *cis*-butadiene. The HOMO of **7b** can approximately be regarded as a combination of the HOMO of **7a** and that of *cis*-butadiene (cf. Figure 2a). This applies as

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Table II. Calculated Bond Lengths of **7a–c** and of *cis*-Butadiene in the Ground State S_0 as well as in the Excited States S_i

Bond[a]	Bond lengths[b]						
	S_0[c]	$S_1{-}S_0$[d]	S_0[c]	$S_1{-}S_0$[d]	S_0	$S_1{-}S_0$[d]	$S_2{-}S_0$[d]
	7a		**7b**		**7c**		
A	1.409	−0.015	1.413	+0.005	1.411	+0.016	+0.004
B	1.388	+0.036	1.389	−0.003	1.390	−0.010	+0.004
C	1.409	−0.015	1.408	+0.012	1.411	+0.016	+0.004
D	1.388	+0.019	1.391	−0.006	1.399	+0.013	+0.014
E	1.416	+0.051	1.411	+0.033	1.406	−0.005	+0.023
F	1.388	+0.019	1.395	−0.007	1.399	+0.013	+0.014
G	1.486	−0.050	1.488	−0.007	1.494	−0.008	−0.028
H	1.486	−0.050	1.493	−0.042	1.494	−0.008	−0.028
	cis-Butadiene						
I			1.467	−0.034	1.467	−0.025	−0.016
J	1.343	+0.090	1.353	+0.040	1.353	+0.025	+0.017
K	1.464	−0.071	1.460	−0.036	1.460	−0.024	−0.016

[a] See Diagram I. [b] In Å. [c] Our values differ from those given in ref. 22 less than 0.01 Å. [d] Difference between the bond lengths of S_i and S_0.
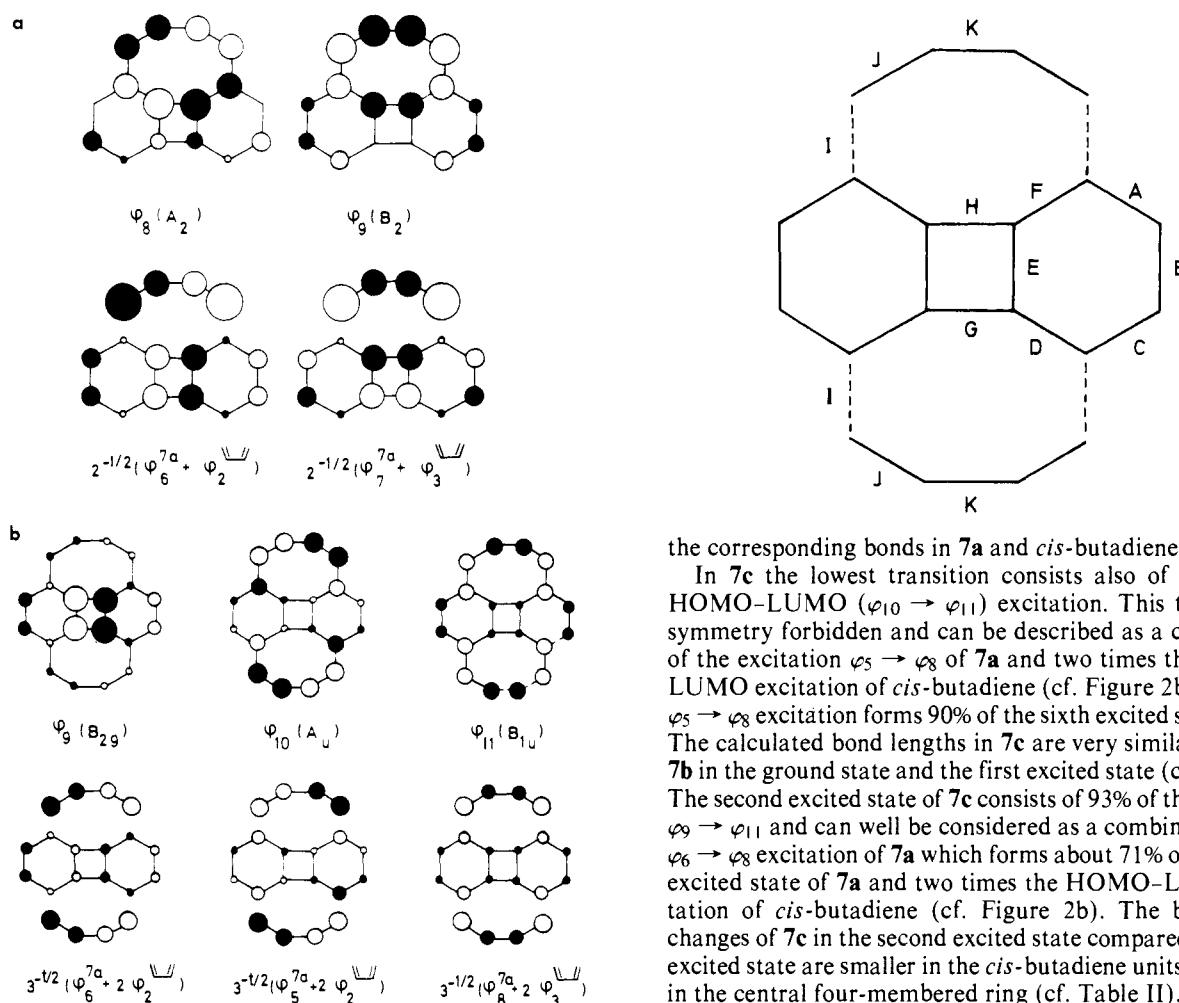
Figure 2. (a) Molecular orbitals φ_8(HOMO) and φ_9(LUMO) of **7b** as well as the normalized linear combinations of the corresponding orbitals of **7a** and *cis*-butadiene. (b) Molecular orbitals φ_9, φ_{10}, and φ_{11} of **7c** as well as the normalized linear combinations of the corresponding orbitals of **7a** and *cis*-butadiene.

well to the LUMO of **7b**. The calculated bond lengths of **7b** in the ground state are very similar (deviations less than 0.01 Å) to the corresponding ones in **7a** and *cis*-butadiene (cf. Table II). The changes of the bond lengths in the 8-membered ring for the lowest transition are, however, smaller in **7b** than for

the corresponding bonds in **7a** and *cis*-butadiene.

In **7c** the lowest transition consists also of 95% of the HOMO–LUMO ($\varphi_{10} \rightarrow \varphi_{11}$) excitation. This transition is symmetry forbidden and can be described as a combination of the excitation $\varphi_5 \rightarrow \varphi_8$ of **7a** and two times the HOMO–LUMO excitation of *cis*-butadiene (cf. Figure 2b). In **7a** the $\varphi_5 \rightarrow \varphi_8$ excitation forms 90% of the sixth excited singlet state. The calculated bond lengths in **7c** are very similar to that of **7b** in the ground state and the first excited state (cf. Table II). The second excited state of **7c** consists of 93% of the excitation $\varphi_9 \rightarrow \varphi_{11}$ and can well be considered as a combination of the $\varphi_6 \rightarrow \varphi_8$ excitation of **7a** which forms about 71% of the second excited state of **7a** and two times the HOMO–LUMO excitation of *cis*-butadiene (cf. Figure 2b). The bond length changes of **7c** in the second excited state compared to the first excited state are smaller in the *cis*-butadiene units but greater in the central four-membered ring (cf. Table II).

The introduction of phenyl groups as in **7e**, **7g**, or **7i** does not lead to significant shifts of the calculated lowest transition energies as in contrast to the benzocyclobutenes **1–6**. The first excited singlet state of **7d** is of the same kind as that of **7b**. The additional annelated cyclobutene increases the extinction coefficient and the transition energy. The first transition energy of **7f** is shifted to a lower energy compared to **7b** and **7d** and its intensity is calculated to be between that of **7b** and **7d**. This transition consists of 83% of the HOMO–LUMO ($\varphi_{11} \rightarrow \varphi_{12}$) excitation and is very similar to a combination of the $\varphi_5 \rightarrow \varphi_8$ excitation of **7a** and of the HOMO–LUMO excitation of *cis*-
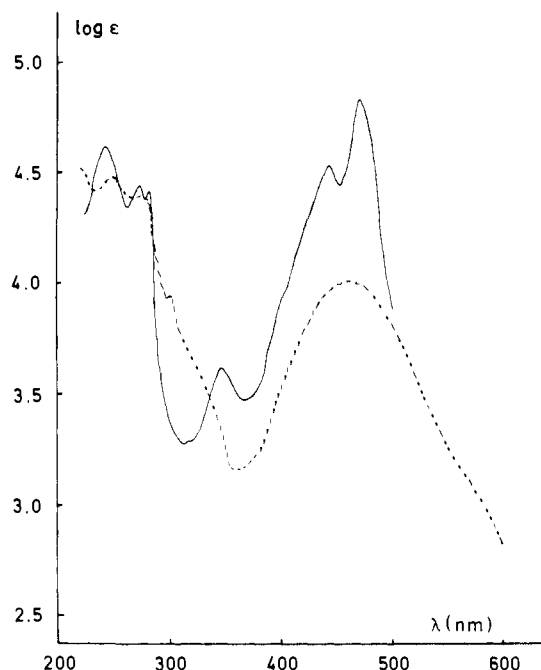
Figure 3. UV–vis spectra of X^{31} (- - -) and 12^{33} (—).

butadiene similar to **7c**. The lowest transition of **7h** is symmetry forbidden and consists of 73% of the HOMO–LUMO ($\varphi_{12} \rightarrow \varphi_{13}$) excitation and corresponds to the lowest transition of **7c**. The second transition consists of 91% of the excitation $\varphi_{11} \rightarrow \varphi_{13}$ and corresponds to the second transition of **7c**.

Phenanthro[1]cyclobutene and Isomer Compounds. 1,2-Diphenylphenanthro[1]cyclobutene (**8b**) is described as an unstable intermediate and it was postulated that it might exist as a triplet in the ground state.[26] This was supported by calculations of Hilpern.[27] However, our calculated triplet state is 0.65 eV above the singlet ground state. This value is certainly a lower bound, since the lowest triplet state of benzene is calculated to be at 2.46 eV compared to the experimental value of 3.95 eV.[28] Bergmann and Agranat[1] reported the attempted synthesis of the triafulvene **9a**. They obtained an unknown compound with molecular weight 354, here abbreviated as X. They tentatively ascribed to this hydrocarbon the formula **8b** although **8b** is characterized as unstable by a graph theoretical investigation[8] or as an intermediate case between stable and unstable structures.[5] They also discussed the other formally possible structures **9b** and **9c**. The calculated transition energies for **9a** and **10** reproduce satisfactory the experimental values. We have to consider that the UV–vis spectra of **9a** and **10** are very solvent dependent because, according to our calculations, the very large dipole moments μ for the ground state (μ = 4.9 D, directed from the three-membered to the five-membered ring in the case of **9a**) and the first excited singlet state (μ = 7.3 D) are opposite in sign.[29] In contrast to **9a** the dipole moment of X is only 0.8 D[1] and the position of the longest wavelength band is practically independent of the solvent. X also cannot have the structure of one of the isomers **9b** and **9c** because of the following reasons.[30] For **9c** we calculate a

dipole moment higher than 2 D. Only for **8b** and **9b** do we obtain lower dipole moments (μ = 0.54 and 0.25 D, respectively). However, the lowest experimental transition energy of **8b** should be smaller and that of **9b** higher than that reported for X. The UV–vis spectrum of $X^{1,31}$ resembles rather that of $11^{32,33}$ (cf. Figure 3). Therefore, we propose for X the structure of the butatriene **12** for which we would also expect a low dipole moment as obtained for X. The NMR spectrum of X is in agreement with the structure of **12**.

HMO calculations[3] indicate that **8c** should be highly unstable and reactive as is **8b**. The lowest transition of **8c** is symmetry forbidden whereas the second transition is allowed and has about the same energy as that of **8b**.

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