Electronic Spectra and Conformations of Some Heterocyclic Derivatives of 5H-Dibenzo(a,d)cycloheptene

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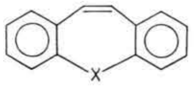
The electronic transitions in 5H-dibenzo(a,d)-cycloheptene (**1**), 5H-dibenz(b,f)azepine (**2**), dibenz(b,f)oxepine (**3**), 5-dibenzo(a,d)cyclohepten-5-one (**4**), dibenzo(b,f)thiepine (**5**) and dibenzo(b,f)selenepine (**6**) have been calculated by the SCF LCAO MO CI method for model conformations and compared with experimental uv absorption spectra. The spectral characteristics and conformations of the title compounds and their relationship to cis-stilbene and o-substituted cis-stilbenes are discussed.

5H-dibenz(b,f)azepine (**2**), dibenz(b,f)oxepine (**3**), dibenzo(a,d) cyclohepten-5-one (**4**), dibenzo-(b,f)thiepine (**5**), and dibenzo(b,f)selenepine (**6**) can be considered as heterocyclic analogs of 5H-dibenzo(a,d)cycloheptene (**1**) obtained by replacing its $-CH_2$-group with the corresponding heteroatoms.



X = CH_2(1); NH(2); O(3);
C=O(4); S(5); Se(6)

Although some derivatives of these compounds have been known for a long time (e. g. a derivative of **2** since 1899 [1a] and of **3** since 1911 [1b]), in recent years these compounds and their derivatives have attained considerable importance because of their pharmaceutical activity [2]. Thus, a systematic investigation of their chemical and physical properties would be of interest. In the present communication we wish to report the results of our studies on the electronic spectra of compounds **1**–**6** which, as we think, also provide some insight into the yet unknown molecular structure.

Abbreviations: SCF, self consistent field; LCAO, linear combination of atomic orbitals; MO, molecular orbital; CI, configuration interaction; PPP, Pariser, Parr and Pople's (Method); HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; CT charge transfer; S_0-T, singlet-triplet; T-T, triplet-triplet.

Method and Results

In the course of these studies the uv spectra of the compounds **1**, **3**, **4** and **5** were recorded (in fact, the spectra of **1**–**6** are known from literature [3]) and theoretical calculations of the electronic spectra of the compounds **1**–**6** were performed using the same set of approximations. These approximations concern the parametrization within the calculation procedure and the geometry of the molecules. We have used the semiempirical SCF MO method of Pariser-Parr [4] and Pople [5] which has been shown to be valuable for the study of electronic spectra of π-electron systems. The formalism of the PPP-method is well known [6] and presented extensively in recent monographs and textbooks. The semiempirical parameters used in the calculations are listed in Table I. Two-center repulsion integrals were calculated by the Mataga-Nishimoto expression [7]. The value of β_{CC} was held the same regardless of the actual bond length. The sulphur and selenium atoms have been considered without participation of d-orbitals. In conclusion, the parametrization within the present calculations could be considered as standard.

More complicated is the problem of the actual structure of these molecules needed for the calculations. It is almost certain that compounds **1**–**6** in their ground states are not planar [3b]. The general deviation from planarity and the numbering used is shown in Figure 1. Nevertheless, we performed a PPP-calculation for each compound in its planar

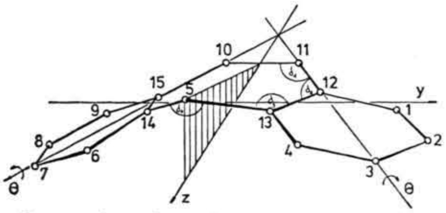


Fig. 1. Proposed conformation, orientation and numbering of atoms and bond angles in the studied 5H-dibenzo(a,d)cycloheptene analogs.

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form using the standard bond lengths as given in Table I. These bond lengths have also been used in the calculation of the nonplanar "boat" forms, but in order to get consistency between bond lengths and angles two approximations concerning the bond angles have been chosen (cf. Figure 1). In the planar seven-membered ring the bond angles are determined by the assumed bond lengths and have values between 115° and 135° for compounds **1** − **6**. Deviation from planarity takes place by a disrotatory motion of the benzene rings by the angle Θ. In both approximations the angles δ_1, δ_2 and δ_3 were taken to be equal. In the first, they were chosen as 120° (corresponding thus to sp²-hybridization of the carbon atoms) and δ_4 is determined by the angle $\Theta\,\mathrm{sp}^2$ and the condition to get the seven-membered ring closed. The resulting values (in degrees) of the angles $\Theta\,\mathrm{sp}^2$ and δ_4 for compounds **1** − **6** are 49.7 and 95.5; 48.7 and 98.7; 46.7 and 100.2; 47.1 and 99.2; 51.0 and 92.4; 53.3 and 92.4 respectively. In the PPP calculations performed for all compounds the same parameters as given above have been used, except that $\beta_{c-\mu}$ for bonds around which the rotation by Θ took place was replaced by [8]

$$\beta'_{c-\mu} = \beta_{c-\mu} \cos \Theta \,.$$

The disadvantage of this approximation is that only one dihedral angle Θ results from it which is probably too high.

In the second approximation, again with $\delta_1 = \delta_2 = \delta_3$ but their value and the resulting value of δ_4

Table I. Summary of Parameters.

Atom	W_{μ^+}/eV	$\gamma_{\mu\mu^+}$/eV	$\beta_{C-\mu}$/eV	$r_{C-\mu}$/Å
Ċ	11.16	11.13	−2.39	1.40 benzenic 1.35 olefinic 1.46−1.50 others
(CH$_2$ inductive)	(14.42)	(13.84)		
N̈	26.70	17.44	−2.49	1.42
Ö	33.00	21.53	−1.80	1.39
Ȯ	19.60	18.89	−2.46	1.24
S̈	22.88	11.90	−2.00	1.72
S̈e	19.17	9.29	−1.43	1.96

Table II. Position (in eV) oscillator strength, polarization and main

Transition		cis-stilbene	1		2	
			Planar	Boat *	Planar	Boat *
1st:	Energy	4.08	3.82	4.45	2.28	3.48
	f	(0.52)	(0.90)	(0.28)	(0.02)	(0.00)
	Polarisation	y	y	y	y	y
	Configuration **	1−1′	1−1′	1−1′	1−1′	1−1′
2nd:	Energy	4.51	4.44	4.69	3.67	4.39
	f	(0.00)	(0.05)	(0.06)	(0.09)	(0.04)
	Polarisation	x, z	z	x, z	y	y
	Configuration **	1−2′, 2−1′	1−2′, 2−1′	1−2′, 2−1′	1−2′, 2−2′	1−2′, 1−1′
3rd:	Energy	4.53	4.58	4.92	4.10	4.48
	f	(0.00)	(0.15)	(0.24)	(0.04)	(0.02)
	Polarisation	y	y	y	z	x, z
	Configuration **	1−3′, 3−1′	1−3′, 3−1′	1−3′, 1−1′	1−3′, 3−1′	1−3′, 3−1′
4th:	Energy	5.37	5.26	5.35	4.61	4.68
	f	(0.00)	(0.00)	(0.01)	(2.08)	(0.03)
	Polarisation	x, z	z	x, z	y	x, z
	Configuration **	1−4′, 4−1′	2−1′, 4−1′	2−1′, 1−2′	2−1′, 1−2′	1−4′, 2−3′
5th:	Energy	5.63	5.67	5.88	4.95	4.69
	f	(0.44)	(0.19)	(0.19)	(0.06)	(0.58)
	Polarisation	y	y	x, z	z	y
	Configuration **	1−3′, 3−1′	3−1′, 1−3′	1−4′, 2−1′	1−4′, 3−1′	2−1′, 1−1′
6th:	Energy	5.69	5.76	5.95	5.51	5.06
	f	(0.00)	(0.01)	(0.09)	(0.17)	(0.01)
	Polarisation	x, z	z	y	z	y
	Configuration **	1−2′, 2−1′	1−4′, 2−1′	1−3′, 3−1′	1−4′, 3−1′	2−2′, 5−1′
7th:	Energy	5.80	5.91	6.16	5.53	5.17
	f	(0.40)	(0.54)	(0.17)	(0.09)	(0.02)
	Polarisation	x, z	z	x, z	y	x, z
	Configuration **	1−4′, 4−1′	4−1′, 1−2′	1−2′, 4−1′	1−5′, 2−2′	1−4′, 3−1′

* Boat corresponds to a rotation for an angle $\Theta\,\mathrm{sp}^2$.

being a function of Θ, the possibility for a continuous change from planar forms to such twisted by any $\Theta \leqq \Theta_{sp^2}$ is given. There is, perhaps, a small difference between the planar forms described above and conformations with $\Theta = 0^\circ$ in this approximation resulting from the equality of the bond angles in the latter case. Calculations have been performed only for **4** with the angles $\Theta = 0^\circ$, 15°, 30° and 45° and the resulting values of δ_1 and δ_4: 128.9° and 126.8°; 128.2° and 124.1°; 126.0° and 115.9°; 121.8° and 101.2°, respectively. In all calculations, after the self-consistency was obtained, a configurational interaction (CI) procedure was started taking into accout all singly excited electronic states. The resulting energies of seven lowest singlet-singlet transitions, their polarization and oscillator strength (in brackets), together with the most important configuration (for notation see Ref. [9]) for planar and nonplanar ("boat") forms of **1**−**6** and cis-stilbene (using the same parameters [Table I] and an angle $\Theta = 30^\circ$) are listed in Table II. A comparison of calculated electronic transitions in the nonplanar forms with actual uv spectra is shown in Figure 2. The correlation of

Table III. Energies of the five lowest lying triplet states (in eV) of compounds **1**−**6** and cis-stilbene.

Compound		T_1	T_2	T_3	T_4	T_5
Cis-stilbene		1.54	2.48	2.75	3.71	3.71
1	Planar	1.32	2.38	2.76	3.50	3.50
	Boat *	1.73	2.37	2.51	3.72	3.72
2	Planar	0.89	2.39	2.47	3.03	3.16
	Boat *	1.70	2.45	2.58	3.48	3.75
3	Planar	1.14	2.43	2.74	3.31	3.51
	Boat *	1.70	2.47	2.62	3.81	3.82
4	Planar	1.05	1.48	2.67	2.81	3.29
	$\Theta = 15^\circ$	1.16	1.51	2.65	2.79	3.34
	$\Theta = 30^\circ$	1.34	1.59	2.55	2.74	3.50
	Boat *	1.46	1.73	2.48	2.62	3.79
5	Planar	1.12	2.45	2.73	3.29	3.52
	Boat *	1.74	2.47	2.58	3.83	3.85
6	Planar	1.19	2.46	2.78	3.32	3.56
	Boat *	1.17	2.47	2.57	3.83	3.86

* Boat corresponds to a rotation for an angle Θ_{sp^2}.

configuration ** of electronic singlet-singlet transitions in **1**−**6** and cis-stilbene.

3		**4**		**5**		**6**	
Planar	Boat *	Planar	Boat *	Planar	Boat *	Planar	Boat *
3.07 (0.20) y $1-1'$	4.43 (0.36) y $1-1'$	3.71 (0.49) y $1-1'$	4.50 (0.02) x, z $1-2', 2-1'$	3.01 (0.22) y $1-1'$	4.51 (0.29) y $1-1'$	3.13 (0.27) y $1-1'$	4.46 (0.15) y $1-1'$
4.08 (0.00) y $1-2', 2-1'$	4.64 (0.01) y $2-1', 1-2'$	3.80 (0.11) z $1-2', 3-1'$	4.52 (0.44) y $1-1'$	4.06 (0.00) y $1-2', 2-1'$	4.68 (0.07) y $1-2', 2-1'$	4.13 (0.04) y $2-1', 1-2'$	4.70 (0.00) x, z $1-3', 3-1'$
4.32 (0.01) z $1-3', 3-1'$	4.65 (0.00) x, z $1-3', 3-1'$	4.33 (0.04) y $2-1', 1-3'$	4.67 (0.02) y $3-1', 1-3'$	4.31 (0.01) z $1-3', 3-1'$	4.69 (0.00) x, z $1-3', 3-1'$	4.32 (0.00) z $1-3', 3-1'$	4.71 (0.10) y $1-2', 2-1'$
4.86 (1.59) y $2-1', 1-2'$	5.36 (0.27) y $6-1', 2-1'$	4.91 (0.17) z $3-1', 1-4'$	4.91 (0.04) x, z $1-2', 1-5'$	4.89 (1.73) y $2-1', 1-2'$	5.57 (0.43) y $2-1', 1-2'$	4.83 (1.58) y $1-2', 2-1'$	5.25 (0.53) y $2-1', 1-2'$
5.13 (0.02) z $1-4', 4-1'$	5.54 (0.00) x, z $1-4', 4-1'$	5.00 (0.34) z $3-2', 2-1'$	5.48 (0.14) y $2-2', 4-2'$	5.13 (0.04) z $1-4', 4-1'$	5.62 (0.00) x, z $1-4', 4-1'$	5.15 (0.07) z $1-4', 4-1'$	5.60 (0.06) x, z $1-4', 2-3'$
5.61 (0.08) z $4-1', 3-1'$	5.79 (0.17) x, z $4-1', 1-4'$	5.15 (0.02) z $2-2', 1-4'$	5.59 (0.00) x, z $4-1', 3-2'$	5.54 (0.31) z $1-4', 4-1'$	5.80 (0.15) x, z $4-1', 1-4'$	5.45 (0.28) z $3-1', 1-3'$	5.74 (0.02) x, z $4-1', 1-3'$
5.64 (0.25) z $3-1', 1-4'$	5.94 (0.19) x, z $1-3', 3-1'$	5.26 (1.36) y $1-3', 2-1'$	5.68 (0.00) x, z $3-2', 1-4'$	5.64 (0.00) z $4-1', 3-1'$	6.02 (0.22) x, z $1-3', 3-1'$	5.63 (0.00) z $4-1', 3-1'$	5.79 (0.10) y $2-2', 1-2'$

** for notation see Ref. 9.

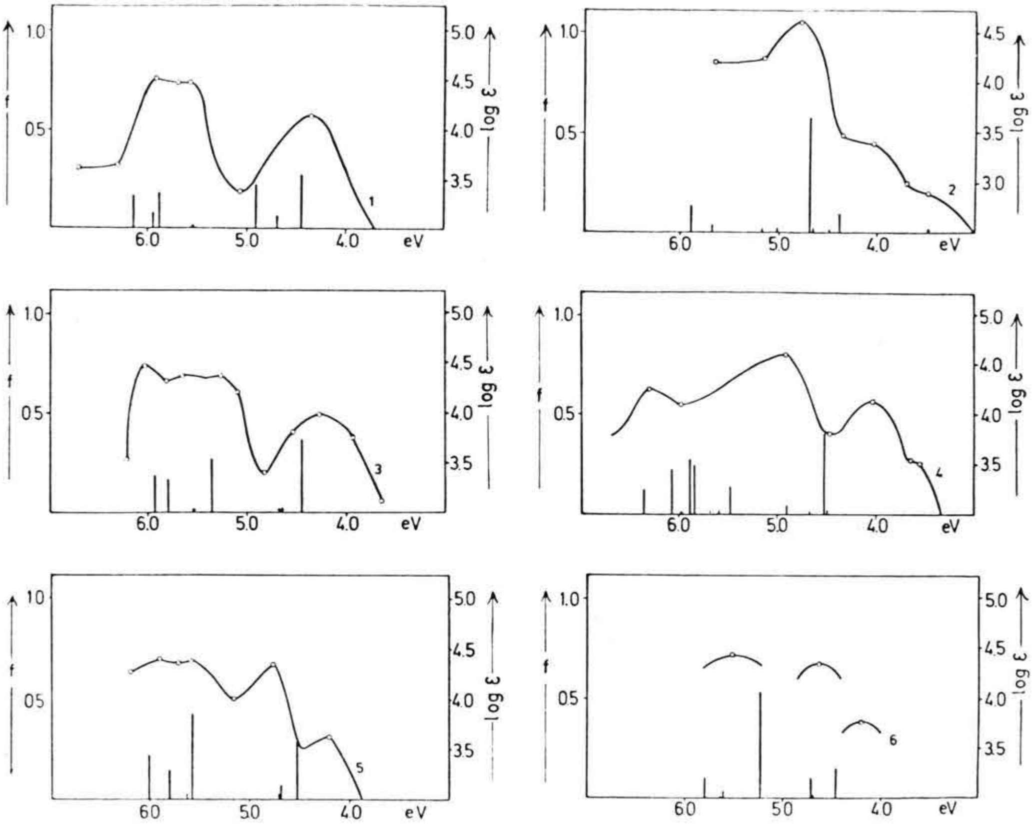


Fig. 2. Comparison of calculated electronic transitions for nonplanar (boat) conformations and uv-spectra (in methanol) of **1**−**6**. Abscissa: Energy in electronvolts. Ordinate: Oscillator strength f. Forbidden transitions are indicated by crosses (spectral data for **2** are from Ref. 3b, for **6** from Ref. 3f).

electronic transitions as functions of Θ with the uv-spectrum of **4**, indicating an experimental angle $\Theta \approx 20^\circ$, is given in Figure 3. The energies of the five lowest lying triplet states calculated for planar and nonplanar forms of **1** − **6** and cis-stilbene are given in Table III.

Discussion

Conformation of 5H-Dibenzo(a,d)cycloheptene Analogs

The geometry of 5H-dibenzo(a,d)cycloheptene and its heterocyclic analogs is still uncertain. Only one preliminary communication[10] concerning the conformation of **4** as studied by x-ray diffraction appeared in 1968 indicating boat conformation with a mutual inclination of the benzene ring planes in the crystall of about 39° (this corresponds to $\Theta = 24.75^\circ$). But there are several indications for nonplanar conformations of **1** − **6**. Cycloheptatriene[11] and some of its derivatives[12] are predicted to be in the boat conformation. From the tempera-

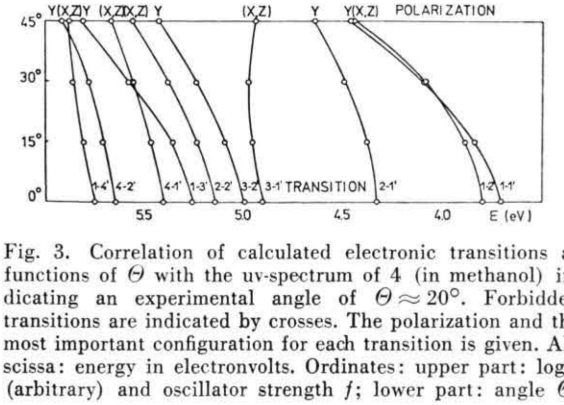
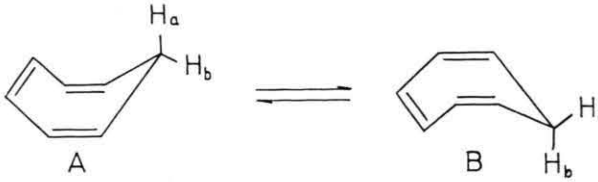


Fig. 3. Correlation of calculated electronic transitions as functions of Θ with the uv-spectrum of 4 (in methanol) indicating an experimental angle of $\Theta \approx 20^\circ$. Forbidden transitions are indicated by crosses. The polarization and the most important configuration for each transition is given. Abscissa: energy in electronvolts. Ordinates: upper part: log ε (arbitrary) and oscillator strength f; lower part: angle Θ.

ture dependence of nmr spectra an activation energy of 6.3 kcal/mol was determined for the transformation of A ⇌ B [11].



Traetteberg [13] investigated by electron diffraction the molecular structure of cycloheptatriene and confirmed the boat conformation.

The activation energy A ⇌ B determined [14] from nmr spectra of 5,5-dimethoxy-tribenzo(a,d,f)cycloheptene amounts to 23 kcal/mol indicating a hindrance caused by the annelated benzene rings (according to Reference [15]). The nmr spectra of **1**, **2**, **3** and **4** exhibit no temperature dependence in contrast to their 10,11-dihydroderivatives, and rigid structures for these compounds have been postulated. Meanwhile recent results [16] indicate a temperature dependence of the nmr spectra of 11-piperazine-**1** down to −60 °C. From a comparison of uv-spectra of N-methyl-**2**, **2**, carbazole and N-methylcarbazole where in the first, but not in the second pair a hypsochromic shift was observed, Huisgen and coworkers [3b] concluded that in contrast to the planar carbazoles the deviation from planarity becomes greater going from **2** to N-methyl-**2**. The observation made by Tochtermann that derivatives of tribenzo(b,d,f)thiepine cannot be resolved into optical antipodes was also explained by their nonplanarity [17].

At present there are no such observations on **6**. The present calculations show that the uv-spectra of **1**−**6** correlate much better with the nonplanar models. The comparison given in Fig. 2 shows a fairly good agreement although indicating that the actual values of Θ might be somewhat smaller. This especially holds for **4**. The correlation of calculated electronic transitions with Θ for **4** as given in Fig. 3 indicates that it should amount to about 20° in good agreement with Reference [10]. Although no such variation of Θ was performed for the other compounds, values of Θ between 30° and 35° can be predicted from the present data.

Electronic Absorption Spectra

As stated above the uv-spectra of the title compounds were known, although for some of them only the extrema are reported. Our spectra of **1**, **3**, **4** and **5** agree with them, except that a maximum at 6.02 eV ($\log \varepsilon = 4.44$) in **3** was not shown in Reference [30]. From Fig. 2 some similarity between the spectra can be deduced but a far greater similarity exists if compared with the corresponding open-systems i.e. cis-stilbene and o-substituted stilbenes in their cis-forms. This similarity has been pointed out in different works many years ago [18, 19] but our calculations show that this similarity is not only a result of the formally similar structure but even more of the same conformation. Namely, cis-stilbene exhibit an angle of twist of about 30° between the benzene rings as it seems to hold for **1**−**6** (20° for **4**). A comparison of electronic transitions for planar and boat forms in Table II, and especially the correlation diagram (Fig. 3) showing the dependence of these transitions with the angle Θ indicates what substantial changes in the shape of the spectrum result from conformation variations. The first transitions are the most sensitive to Θ. Thus, going from planar forms to such with Θ sp^2, hypsochromic shifts of 0.63, 1.20, 1.36, 0.79 and 1.33 eV are predicted for **1**−**6**, respectively. This longest wavelength absorption system in all compounds corresponds mainly (more than 80%) to the $1-1'$ excitation i.e. to the HOMO-LUMO transition (only in **4** an interchange with the second transition at $\Theta \approx 25°$ takes place, see Figure 3). This band is polarized along the long axis (y) of the molecule and in the case of heterosubstitution has significant charge transfer character. The CT-character of this system in 5H-dibenz(b,f)azepine was previously proposed and discussed by Schmid [20] and recently by Kricka and coworkers [21]. Transitions polarized along the short axis (z) in molecules **1**−**6** are mainly forbidden or of a small oscillator strength. For the energies of triplet states listed for all compounds in Table III there is at present no experimental evidence. Neither S_0-T nor $T-T$ spectra have been measured so far. In their triplet states the molecules might have planar conformations.

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