Electronic Spectra and Conformational States of Mono- and Diphenyl Derivatives of [2.2]Paracyclophane

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Ultraviolet spectra of 4-phenyl-[2.2]paracyclophane and of the 4,7- and 4,13-diphenyl derivatives were interpreted. MINDO/3 total molecular energy and *PPP*—CI-1 energies of singlet transitions were calculated for different values of the dihedral angle of the phenyl ring with respect to the benzene ring of paracyclophane. Although most of the theoretical transitions correspond to local excitation within the *PCP* fragment, some of them result in a transfer of electron charge to the phenyl substituents.

Elektronenspektren und Konformationen von Mono- und Diphenylderivaten des [2.2]Paracyclophans

Es werden die UV-Spektren von 4-Phenyl-[2.2]paracyclophan, 4,7- und 4,13-Diphenyl-[2.2]paracyclophan interpretiert. Für verschiedene Dieder-winkel der Phenylringe relativ zu dem Benzolring des Paracyclophans wurden MINDO/3-Rechnungen für die Gesamtenergie und *PPP*—CI-1 Rechnungen für die Singlet-Übergänge durchgeführt. Die meisten der berechneten Über-gänge gehören zu lokalen Anregungen innerhalb des *PCP*-Fragments, einige sind jedoch einem Elektronentransfer zu den Phenylsubstituenten zu-zuschreiben.

Introduction

In this communication we present theoretical considerations con-cerning the conformations of some phenyl derivatives of [2.2]para-cyclophane, *PCP*, and the interpretation of their UV spectra based on

calculations of the electronic transition energies. The compounds under consideration were: 4-phenyl-[2.2]paracyclophane, **A**, 4,7-diphenyl-[2.2]paracyclophane, **B**, and 4,13-[2.2]paracyclophane, **C**, obtained recently in this laboratory[1,2], Fig. 1.

Theoretical interpretation of the electronic spectra of layer compounds like derivatives of [2.2]paracyclophane or some of the

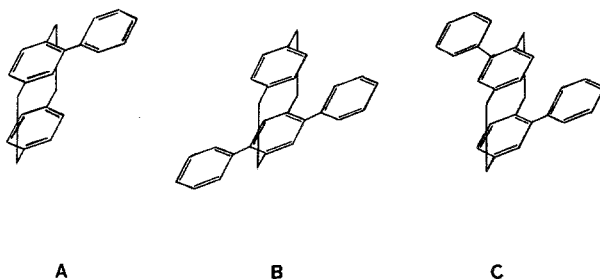   **A**   **B**   **C**

Fig. 1. Investigated phenyl derivatives of [2.2]paracyclophane: A 4-phenyl-[2.2]paracyclophane; B 4,7-diphenyl-[2.2]paracyclophane; C 4,13-diphenyl-[2.2]paracyclophane; the boat-shaped configuration of the benzene rings in the *PCP* fragment is not shown

charge transfer complexes usually encounters some difficulties[3–5]. There are two major factors responsible for this. First, the considered molecules are composed of the two fragments, lying one above other, and each of them representing a π-electron and often aromatic structure. They exhibit a strong transanular interaction affecting both the geometry and spectroscopic properties of the molecule[6–10]. This makes the proper estimation of the interaction energy between two π-electron moieties (a problem so important in the quantum-chemical approach) even more important. The other objection, potentially more dangerous for the standard π-electron approaches to the considered class of compounds is the fact that a pure electronic treatment, based on the *Born-Oppenheimer* approximation, *B—O*, is not always applicable to the dimers or the dimer-like structures. Electronic spectra of such compounds are affected by the vibronic couplings. However, in the case of *PCP* and its derivatives, so called strong coupling occurs which, in fact, affects the *B—O* transition energies only to a minor extent. Moreover, when only energies of the transitions, not their oscillator strengths are considered, it is possible to incorporate the vibronic effects into the π-electron treatment by an appropriate

parametrisation of the resonance integrals between both π-electron components of the molecule.

In view of this, it can be easily recognized that the most important step in the theoretical treatment of the title compounds is to choose a proper procedure to estimate resonance and *Coulomb* integrals involving orbitals belonging to the different π-electron moities. The authors' experience based on previous papers[3, 8] points out that the most suitable are those parametrisations which express one- and two-electron integrals in terms of the overlap integrals, e.g. *Hinze-Beveridge, H—B,* parametrisation[11]. A slightly modified version of the original *H—B* parametrisation was proposed[8], which proved to be particularly useful in predicting electronic spectra of the cyclophane type compounds. Although this procedure of determination of resonance integral admits a new empirical parameter, it appears fully justified in view of the thorough discussion of this problem focused on the layer-type structures presented recently by *Vogler*[12].

Materials and Methods

The phenyl derivatives of [2.2]paracyclophane were obtained according to Ref.[1, 2]: 4-phenyl-[2.2]paracyclophane, m.p. 114–116 °C, 4,7-diphenyl-[2.2]paracyclophane (melts with decomp.) and 4,13-diphenyl-[2.2]paracyclophane, m.p. 158-160 °C. The UV spectra were recorded in 95% ethanol on a Cary 118 spectrophotometer and on a Specord UV-VIS C. Zeiss instrument.

Calculations of the singlet transition energies were carried out by an SCF method in the *PPP*—CI-1 approximation with *Hinze-Beveridge* parametrisation[11]. All details of parametrisation are given elsewhere[8]. Here we consider only the problem of the parametrisation of the resonance integrals. In the *H*—B approximation the resonance integral β_{ij} is given by

$$\beta_{ij} = 0.5\,(Z_i + Z_j)\,S_{ij}(\gamma_{ij} - 2\,C/r_{ij}) \tag{1}$$

where Z_i, Z_j denote the number of π-electrons in the center i and j, S_{ij} and γ_{ij} are the overlap and *Coulomb* two-center integrals, respectively, and r_{ij} is the distance between centers i and j.

A typical feature of that kind of approximation for the resonance integral is the presence of parameter C in the formula. In the original *H—B* approximation $C_{H—B}$ is equal to 0.545. However, in our recent application[3, 8] the value of C was differentiated depending on the type of the orbitals involved in the β_{ij} integral. In the present calculations we also followed that scheme and assume: $C = C_{H—B}$ for all orbitals belonging to the same aromatic unit; $C = 5\,C_{H—B}$ for orbitals belonging to different benzene units of *PCP* or for those belonging to a phenyl substituent and a not adjacent benzene ring of *PCP*; $C = 1.1\,C_{H—B}$ for orbitals belonging to a phenyl substituent and an adjacent benzene ring of *PCP*. (The value of 1.1 was used because it reproduces correctly the UV spectrum of biphenyl in which the dihedral angle is 42°, see Fig. 3).

Rotation of the phenyl substituent with respect to the adjacent benzene unit of *PCP* is taken into account by the fact that the resonance integral is proportional to the corresponding overlap integral between p_z orbitals. The latter is calculated assuming that p_z orbitals are perpendicular to the benzene unit. In other words, they rotate together with the rotating phenyl fragment.

The geometry of considered molecules was adopted from benzene, biphenyl[13] and *PCP*[14, 15]. Interplanar distance in *PCP* was assumed to be 3.11 Å, interring CC bond between phenyl and *PCP* was adopted to be equal to 1.49 Å. In the CI part of the calculation, 40 and 50 singly excited configurations were taken into account for mono- and diphenyl derivatives, respectively. Energies of the singlet transitions were calculated for different values of the dihedral angle φ. To fix the optimum value of the dihedral angle, the total molecular energy vs. dihedral angle φ was calculated by the MINDO/3 method.

Results

The simple model consideration of the investigated compounds shows that one can expect neither a planar conformation nor a perpendicular one of the phenyl ring(s); the stable conformation is resultant of three factors: (i) π-electron interaction with the adjacent benzene ring of *PCP*, (ii) π-electron interactions with the second benzene ring of *PCP*, and (iii) repulsion with the hydrogen atoms of the methylene bridges, interaction H_a—H_b, Fig. 2. The calculated dependence of the total molecular energy on the dihedral angle φ is shown in Fig. 2. It appeared that one should expect two stable conformations: the first one with lowest energy occurs at $\varphi_0 = 48°$, the second one at $\varphi_1 = 113°$. Additional calculations showed that the values of φ_0 and φ_1 are practically insensitive to the assumed values of the other structural parameters, like the length of the interring C_1—C_2 bond or the value of the adjacent C_1—C_2—C_3 angle, see Fig. 2. It may be stated that so called relaxation effects will not change the estimated optimum values of φ_0, although they affect rather strongly the values of the molecular energy of the conformers. The difference between molecular energies of the two stable conformers is equal to 12.7 kcal/mol. The barrier of rotation occuring at 93° is equal to 19.3 kcal/mol with respect to the φ_1 conformer, and 6.6 kcal/mol with respect to the φ_0 conformer. The rather high value of the second barrier of rotation at 0°, i.e. for the planar conformation, may be substantially lowered by the mentioned relaxation effects. The same conformations of phenyl rings were adopted for the diphenyl derivatives of *PCP*.

The conformational analysis results obtained by the direct energy calculation can be compared with the conclusions drawn from the conformational dependence of the UV spectra. Fig. 3 shows the dependence of the energy of the first intense band on the dihedral angle φ_0. For all molecules a maximum batochromic effect is observed when
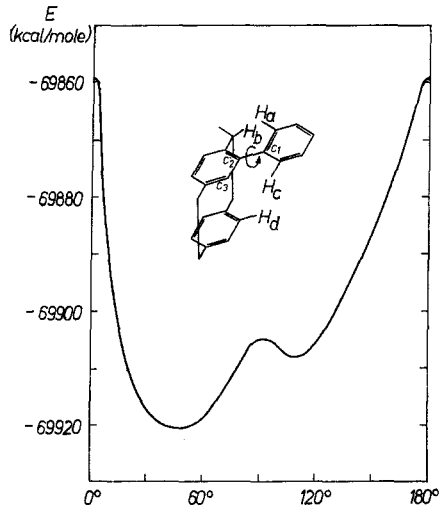
Fig. 2. MINDO/3 molecular energy *vs.* dihedral angle of the phenyl ring in
4-phenyl-[2.2]paracyclophane
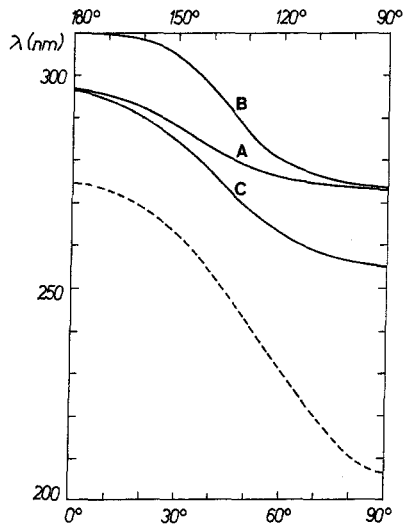

Fig. 3. Energy of the first intense singlet transition *vs.* the dihedral angle of
phenyl ring (*PPP*—CI-1 results) for the phenyl derivatives of [2.2]para-
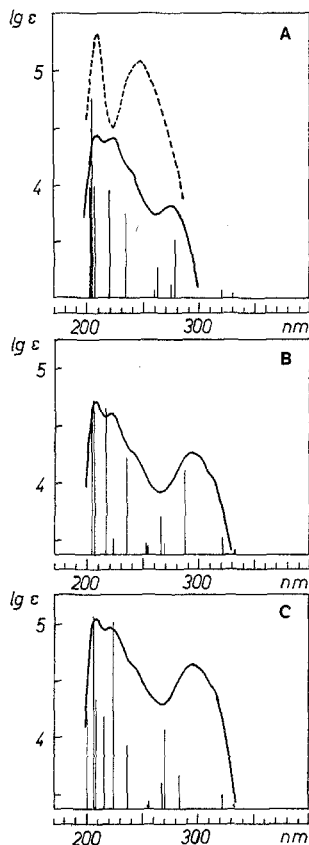cyclophane shown in Fig. 1; the dashed line represents biphenyl

Fig. 4. The experimental spectra of phenyl derivatives of [2.2]paracyclophane (in 95% ethanol) and the theoretical singlet transition energies according to *PPP*—CI-1; theoretical values refer to the most stable (MINDO/3) conformation; the dashed line represents the experimental spectrum of biphenyl

the conformation of the phenyl rings approaches 90°. It should be noted that two conformations correspond to the experimental energy of UV transition, e.g. for 4-phenyl-[2.2]paracyclophane φ_0 is approximately equal to 60°, φ_1 to 120°. Thus, both conformations predicted by UV spectra are equally deviating from planarity.

The interpretation of the UV spectra is given in Tabs. 1-3 and in Figs. 4 and 5. Experimental spectra show three maxima at 276, 222 and 206 nm for compound **A**, at 294, 220 and 207 nm for **B** and at 294, 221 and 206 nm for **C**. Some of them are accompanied by shoulders: at
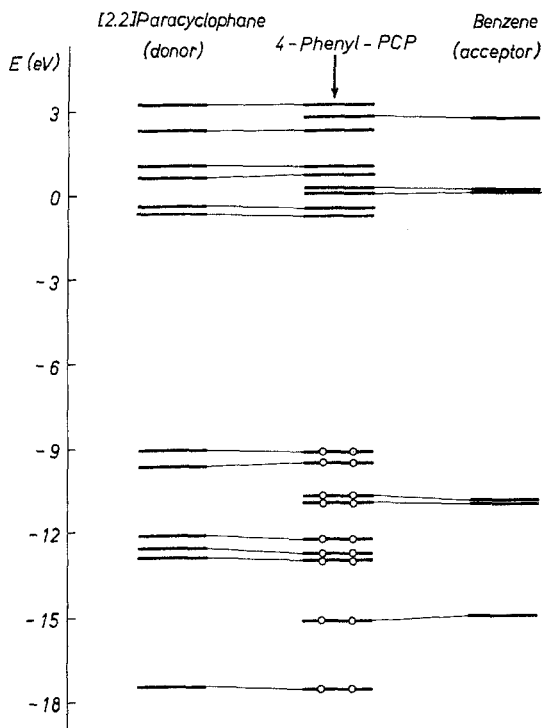
Fig. 5. Correlation diagram of 4-phenyl-[2.2]paracyclophane

238 nm for **A**, at 306 and 240 nm for **B** and at 306 and 241 for **C**. The theoretical results are in very satisfactory agreement with the experimental data for molecules **A** and **B** and a little less for molecule **C**, because according to the calculation the first maximum in the latter compound is shifted towards a shorter wavelength region.

Discussion

Formally, any phenyl derivative of *PCP* can be regarded as an intramolecular CT complex with *PCP* being a donor fragment and phenyl substituent(s) an acceptor. From this standpoint in Tabs. 1–3 characteristics of the theoretical transitions are given, indicating localization of the excitation[16]. To the first observed band in the monophenyl derivative, the 276 nm maximum, four theoretical transitions were assigned, but only two of them show sufficient

Table 1. Experimental and theoretical UV transition energies for 4-phenyl-[2.2]paracyclophane

No.	Sym.	Energy, nm Exp.	Calc.	Oscillator strenght calc.	Assignment[a]	Characteristics[b] DD	AA	DA	AD	ΔQ
1	A		331.6	0.036	LE (D*)	0.755	0.013	0.172	0.600	0.0076
2	A		320.9	0.056	LE (D*)	0.804	0.007	0.156	0.033	0.0043
3	A	276	278.9	0.386	LE (D*)	0.759	0.022	0.142	0.077	0.0371
4	A		276.3	0.096	LE (D*)	0.591	0.023	0.306	0.079	0.0022
5	A		262.9	0.218	LE (D*)	0.732	0.030	0.140	0.098	0.0192
6	A		260.5	0.051	LE (A*)	0.119	0.312	0.248	0.320	0.0633
7	A	238 sh	233.8	0.599	LE (D*) + CT (D1—A)	0.427	0.060	0.400	0.114	0.1154
8	A	222	219.1	0.763	LE (D*)	0.554	0.126	0.164	0.156	0.0893
9	A		206.2	0.784	LE (D*) + CT (D—A)	0.408	0.126	0.342	0.123	0.3193
10	A	206	203.8	1.510	LE (D*) + CT (D1—A)	0.351	0.244	0.258	0.147	0.1281
11	A		202.2	0.769	CT (D—A) + LE (D*)	0.274	0.109	0.457	0.160	0.5882

[a] LE (D*) and LE (A*) denote local excitation within donor (PCP) and acceptor (Ph) fragments, respectively. CT denotes excitations from donor to acceptor, in particular: CT (D—A)—excitations from donor (PCP fragment regarded as a whole) to acceptor, CT (D1—A)—excidations from the benzene ring of PCP (to which phenyl is connected) to acceptor.
[b] Participations of four types of transitions in electronic transitions; the symbols denote as follows: DD-transition within donor, AA — within acceptor, DA — from donor to acceptor, AD — from acceptor to donor; ΔQ gives the charge transferred during the excitation.

Table 2. Experimental and theoretical UV transition energies for 4,7-diphenyl-[2.2]paracyclophane (for footnotes see Table 1)

No.	Sym.	Energy, nm Exp.	Calc.	Oscillator strength calc.	Assignment[a]	Characteristics[b] DD	AA	DA	AD	ΔQ
1	B		333.0	0.035	LE (D*)	0.707	0.024	0.173	0.100	0.0003
2	B	306 sh	322.5	0.132	LE (D*)	0.688	0.024	0.212	0.076	0.0139
3	B	294	287.4	0.711	LE (D*)	0.642	0.055	0.212	0.091	0.0281
4	B		269.3	0.079	LE (D*)	0.512	0.047	0.315	0.126	0.0500
5	B		266.6	0.315	LE (D*)	0.718	0.025	0.144	0.113	0.0246
6	B		252.9	0.056	LE (A*) + CT (D1—A)	0.124	0.487	0.217	0.172	0.1036
7	A		252.5	0.078	LE (A*) + CT (D1—A)	0.015	0.450	0.313	0.223	0.0998
8	B	240 sh	233.7	0.816	LE (D*)	0.397	0.115	0.384	0.104	0.0557
9	A		224.1	0.122	CT (D1—A) + LE (A*)	0.034	0.263	0.535	0.168	0.3236
10	B	220	216.6	1.279	LE (D*) + LE (A*)	0.491	0.202	0.168	0.139	0.0612
11	B	207	207.4	1.383	LE (A*) + LE (D*)	0.281	0.400	0.147	0.171	0.0095
12	B		206.3	1.123	LE (D*) + CT (D1—A)	0.404	0.212	0.257	0.128	0.1148
13	A		202.5	0.011	CT (D—A)	0.041	0.156	0.743	0.060	0.7440

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Table 3. Experimental and theoretical UV transition energies for 4,13-diphenyl-[2.2]paracyclophane (for footnotes see Table 1)

No.	Sym.	Energy, nm Exp.	Energy, nm Calc.	Oscillator strength calc.	Assignment[a]	Characteristics[b] DD	AA	DA	AD	ΔQ
1	A		393.2	0.004	LE (D*)	0.616	0.028	0.263	0.092	0.0078
2	B		322.4	0.095	LE (D*)	0.772	0.012	0.168	0.048	0.0057
3	A	306 sh	383.0	0.210	LE (D*)	0.656	0.034	0.194	0.115	0.0114
4	B	294	270.2	0.557	LE (D*)	0.524	0.071	0.283	0.122	0.0096
5	B		268.5	0.175	LE (D*)	0.516	0.039	0.331	0.114	0.0507
6	A		256.7	0.040	LE (A*) + CT (D—A)	0.033	0.439	0.280	0.248	0.1200
7	B		255.7	0.022	LE (A*) + CT (D—A)	0.019	0.437	0.290	0.255	0.1159
8	A	241 sh	235.1	0.432	LE (D*) + CT (D—A)	0.397	0.110	0.366	0.127	0.0903
9	B	221	225.3	1.314	LE (D*) + CT (D—A)	0.304	0.143	0.312	0.241	0.1325
10	A		215.9	0.652	LE (D*) + LE (A*)	0.427	0.226	0.192	0.155	0.0943
11	A		208.8	0.771	CT (D—A) + LE (D*)	0.321	0.222	0.349	0.108	0.2480
12	B	206	207.3	1.326	LE (A*) + LE (D*)	0.198	0.571	0.102	0.120	0.0073
13	A		200.4	0.646	CT (D—A)	0.055	0.153	0.623	0.169	0.5554

intensity to be observed in the spectrum. Similarly the second band, the 222 nm maximum plus shoulder at 238 nm, correspond to two intensive transitions at 233.8 and 219.1 nm. Most of the theoretical transitions correspond to local excitation within a donor part i.e. the *PCP* fragment. Some of them, however, exhibit high participation of the CT-like transition resulting in a transfer of an electron charge from the *PCP* fragment to the phenyl substituent, e.g. theoretical maxima at 233.8, 206.2, and 203.8 nm in the monophenyl derivative. In diphenyl derivatives there are two bands which exhibit predominant CT character: 224.1, 202.5 nm in compound **B** and 208,8, 200.4 in **C**. Several others are of mixed CT and LE character. In all three compounds there are few theoretical maxima localized in the acceptor part, i.e. in the phenyl fragment. In the mono-derivative there is one wavelength of that character at 260.5 nm and four in each diphenyl derivative (Tab. 2 and 3).

Analysing the electronic spectra of the considered molecules from the point of view of their components we can emphasize the following points. In all cases several bands appear which can be easily retrieved in the spectrum of *PCP*. For instance, bands at 262.9 nm (**A**), 266.6 nm (**B**), 268.5 nm (**C**) correspond to the 254 nm band of *PCP*. Similarly, shoulders at 233.8 nm (**A**), 233.7 nm (**B**) and 235.1 nm (**C**) refer to the weak band at 232 nm in *PCP*, and the bands at 219.1 nm (**A**), 216.6 nm (**B**) and 225.3 nm (**C**) can be ascribed to the 223 nm band of *PCP*. Analysis of the maxima at 260.5 nm (**A**), ca. 253 nm (**B**) and ca. 256 nm (**C**) shows that they have to be identical with the nonactive transition in the benzene molecule at 254 nm; the other benzene transition, 204 nm, can be recognized in the ca. 207 nm maximum in the **B** and **C** derivatives.

The similarity of the spectra of the [2.2 paracyclophane] derivatives with those of the parent molecule can be explained by comparing their orbital energies (Fig. 5). Each orbital level of the 4-phenyl derivative can be ascribed to a corresponding orbital level of its components.

Owing to the twisted conformation of the phenyl ring with respect to *PCP* one cannot expect any extended delocalization of π-electrons between them. That is the main reason why the general electronic structure of a *PCP* derivative retains many features of that of the parent molecule.

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