Electronic Structure Calculations of a Chiral [2.2]Metacyclophane

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Qualitative and semi-empirical MO theory is employed in an attempt to interprete the CD spectrum of triphenylenicene (1), a chiral [2.2]metacyclophane. There is over-all agreement in the description of states; however, through-space interaction of the aromatic chromophores causes rotation of certain electric transition moments, which results in peculiar, but logical changes of calculated rotational strengths. The absolute configuration of (−)-1 is assigned M helicity, in contrast to previous assumption.

Berechnungen der elektronischen Struktur eines chiralen [2.2]Metacyclophans

Qualitative und semiempirische MO-Theorie werden eingesetzt, um das CD-Spektrum eines chiralen [2.2]Metacyclophans, Triphenylenicen (1), zu interpretieren. Die Modelle liefern eine im Ganzen übereinstimmende Beschreibung der Zustände. Die Wechselwirkung der aromatischen Chromophore durch den Raum führt jedoch zu einer Verdrehung bestimmter elektrischer Übergangsmomente, was die berechneten Rotationsstärken in einer besonderen, aber verständlichen Weise verändert. Der absoluten Konfiguration von (−)-1 wird M-Helizität zugeschrieben, im Gegensatz zur bisherigen Annahme.

In 1980, Vögtle and Hammerschmidt reported the synthesis of benzo[2.2]metacyclophane (triphenylenicene, 1), a chiral hydrocarbon[1]. It was resolved three years later and its X-ray structure determined[2]. From a comparison of its chiroptical properties with those of a helicene of known absolute configuration, 2, the probable absolute configuration of (−)-1 was assumed to be P[3].

With point group C_2, triphenylenicene is high-symmetry chiral[4], like the biphenyls[5], the 1,1′-binaphthyls[6] and -bianthryls[7], or certain cyclophanes[8], to name but a few. Not only is the symmetry in these compounds of considerable help in describing their electronic structure; if the geometry-dependent interaction of degenerate excited states results in what is generally known as exciton interaction[9], the absolute configuration can be assigned often with high reliability from spectroscopic measurements and a qualitative picture of the excited states.

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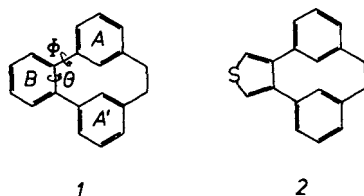
At first glance, triphenylenicene with its inherent chirality seems an easy target for this kind of analysis. It will be seen, however, that due to the special bonding situation present in this compound, the qualitative MO picture of the molecule is probably wrong. PPP calculations improve the description, but only on the basis of CNDO results can the CD spectrum be rationalized. Based on this analysis, we arrive at an absolute configuration which differs from the one previously accepted.

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Geometry Calculations

The CD spectrum of chiral 1 above 210 nm[2] is made up of at least three bands centered at 225, 250, and 300 nm, respectively. It is almost temperature-independent (Figure 1), indicating the predominance of one rather rigid solution conformation, probably the one also found in the crystal[2].
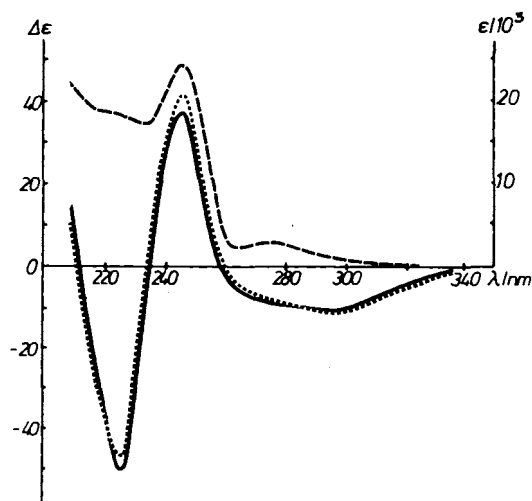
Figure 1. Electronic spectra of (−)-1
(− − −): room temperature, UV; (———): room temperature, CD;
(·······): −120°, CD

To corroborate the latter assumption, force-field calculations employing the MMP2 scheme were performed. The resulting minimum energy conformation is shown in Figure 2. Calculated bond lengths and angles and dihedral angles agree extraordinarily well with experimental values.

Chirality results from the out-of-plane twist of the two aromatic rings A and A′ against the plane of the annulated ring B, giving the whole molecule C_2 symmetry. The twist
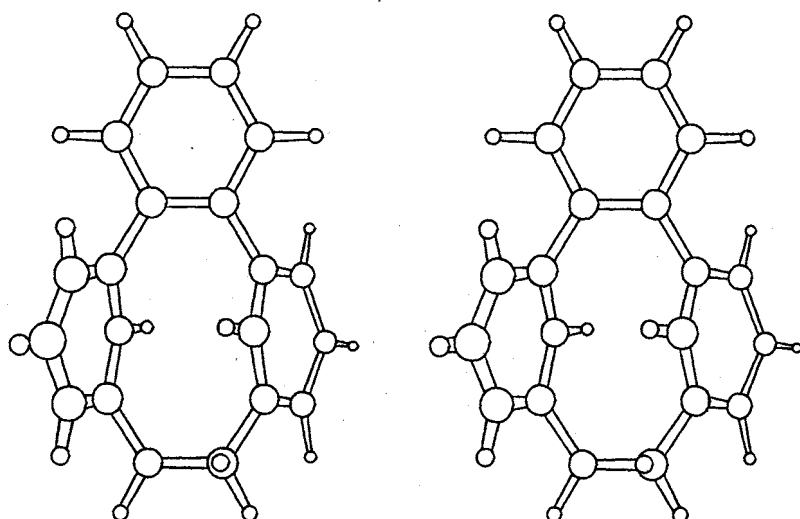
Figure 2. Stereoplot of MMP2 minimum energy conformation of **1**. Absolute configuration shown corresponds to *M* helicity

angle Φ, with a calculated value of 44° (experimental 41 and 44°), is positive for *P*, negative for *M* helicity. In addition, the *ortho*-bridges of ring B are twisted against each other by 10° (11° experimental), the twist angle, Θ, being positive for *M* and negative for *P* helicity. The chiroptical properties of **1** depend primarily on these two angles. While ring B is almost planar, A and A′ are slightly boat-like deformed, again in agreement with the X-ray results.

Electronic Structure; Qualitative MO Picture

A qualitative understanding of the MOs and resulting electronic states of **1** may be obtained by considering only the frontier orbitals of the three benzene chromophores and their interactions as depicted in Figure 3. After combining the orbitals on rings A and A′ into symmetry-adapted group orbitals, there result, in order of increasing energy, the bonding (2A and 3B, not shown), non-bonding (3A and 4B), and anti-bonding combinations (5B and 4A) of the HOMOs and the bonding (5A and 6B), non-bonding (6A and 7B) and anti-bonding combinations (8B and 7A, not shown either) of the LUMOs of the contributing benzene units. The important relative ordering, 4A < 5B and 5A < 6B, which makes 5B and 5A the HOMO and LUMO, respectively, of the whole molecule, is due to the fact that in each pair of degenerate MOs on ring B, the MO with the larger coefficient at the junction can interact more strongly with the group orbital of corresponding symmetry. The degeneracy of 3A and 4B, and of 6A and 7B, respectively, which neglects the close proximity of rings A and A′, cannot be expected to hold in more sophisticated calculations, and if it were only for the fact that the actual symmetry of the molecule (C_2) does not allow any degeneracy.

The electronic states derived from these MOs may be conveniently grouped according to their energies and orientation of transition moments. Polarization diagrams and estimates of oscillator and rotational strengths are given in Table 1.

i) *Low-Energy States.* These involve MOs 4A through 6B whose interactions give rise to four singly excited configurations. They are characterized by strong participation of
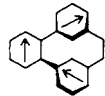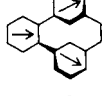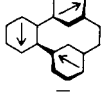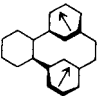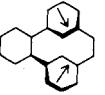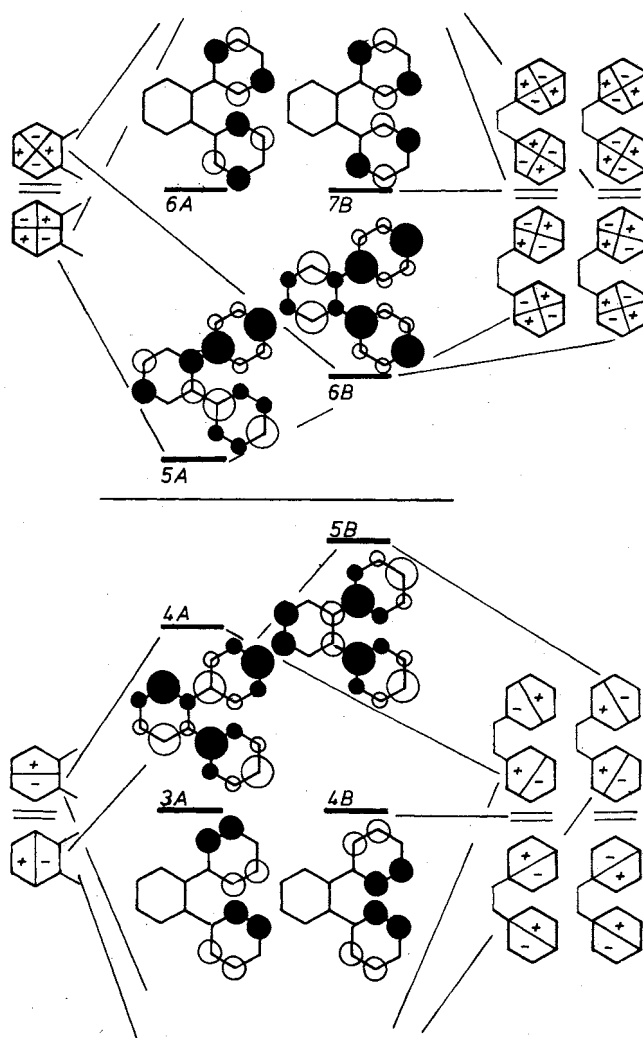

Figure 3. Qualitative MO diagram of the π system of **1** resulting from the interaction of three benzene units. Labelling according to C_2 symmetry; only frontier orbitals are shown

ring B and long-axis polarization of A and A′ (Table 1). Configuration interaction (CI) is expected to strongly mix the configurations of A symmetry (4A — 5A and 5B — 6B),

leading to a low-energy forbidden and a high-energy, high-intensity state. CI between the B states is probably negligeable.

Table 1. Qualitative MO results for 1 with M helicity

Configuration	Symmetry	Polarization	Oscillator strength	Rotational strength
5B−5A	B		small	>0
(4A−5A) −(5B−6B)	A⁻		−	−
(4A−5A) +(5B−6B)	A⁺		large	<0
4A−6B	B		small	small
(5B−6A) −(4B−5A)	B⁻		−	−
(5B−7B) −(3A−5A)	A⁻		−	−
(5B−6A) +(4B−5A)	B⁺		large	<0
(5B−7B) +(3A−5A)	A⁺		small	>0

For this "4-orbital model" a close analogy can be drawn to the MO description of conjugated polyenes[10]. The two low-energy states of A and B symmetry correspond, respectively, to the forbidden but possibly lowest[11] and to the strongly allowed $\pi\pi^*$ state (A_g^- and B_u^+ in a planar, *all-trans* polyene, point group C_{2h}), while the high-energy A state corresponds to the so-called *cis* peak (A_g^+ in C_{2h}), which gains intensity only through a *cis* linkage in the chromophore[12].

For exact long-axis polarization, the rotational strengths associated with these states depend only on the value of Θ, not on Φ. The polarization diagrams of these states show that the relative orientation of electric and magnetic transition moments is such as to lead to positive rotational strengths for the B states, and to negative ones for the A states. This conforms with the diene helicity rule[13] according to which positive CD absorption is expected for the long-wavelength transition of a P-twisted diene and negative rotatory strength for the *cis* peak.

ii) *Short-Axis Polarized States.* These states involve the two sets of degenerate A,A'-group orbitals, either from or into which an electron is excited. The configurations come as degenerate pairs, e.g. 5B−6A, 4B−5A or 3A−5A, 5B−7B, which after CI are split into forbidden low-energy B⁻ and A⁻ and allowed high-energy A⁺ and B⁺ states, respectively. The polarization of these states, which have intensity only in the A and A' rings, is short-axis (Table 1),

which makes the rotational strengths derived from them depend on both Θ and Φ. For states of B symmetry, they should be negative, for A symmetry positive.

With increasing energy, interaction between different configurations is likely to gain in importance. CI is expected to affect all states of like symmetry.

The assignment of the three bands in the experimental spectrum at 300, 250, and 240 nm to the low-energy B, A⁺ and B⁺ states, respectively, appears most probable from energy and intensity considerations. With regard to rotational strengths, a +,−,− sequence of signs is expected for 1 with M helicity, while the experimental sequence is +,−,+ (or −,+,−). No assignment of absolute configuration is possible on the basis of this simple MO picture.

PPP Calculations

The PPP input was modified in view of the special bonding situation found in 1. To account for the twist of the aromatic rings against each other, the resonance integral between adjoining ring centers was reduced by a factor of .8, this arbitrary value being chosen only in order to study its effect on the calculations. Furthermore, the close proximity of rings A and A' was simulated by introducing a partial bond between the intraannular carbon atoms. Because of Möbius-type overlap involved, a positive resonance integral ($-.4\beta$) was chosen which results in a bonding situation if there is sign inversion across the bond.

As a consequence of the extra bond, the local transition moments on rings A and A' can no longer be classified as purely long-axis or short-axis polarized. Instead, they are rotated, the sense of rotation being determined by the special type of bond chosen. Figure 4 illustrates, how as a consequence there results an additional component of rotational strength, with sign critically dependent on the relativ disposition of the transition moments.

The CI diagram of the PPP calculation (Figure 5) completely agrees with the qualitative arguments developed in
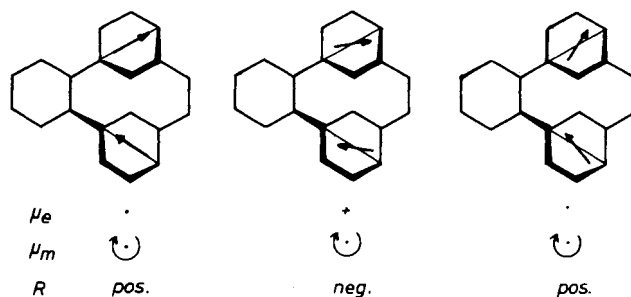
Figure 4. Effect of rotating the HOMO−LUMO transition moments on calculated rotational strength. Coupling of the moments leads to clockwise charge rotation, with the magnetic moment μ_m pointing away from the observer. For transition moments exactly long-axis polarized (left), the positive twist due to Θ results in an electric moment μ_e pointing in the same direction and leading to positive rotational strength R. Clockwise rotation of the transition moments (middle) adds an electric moment in the opposite direction due to the negative twist of Φ, resulting in a negative component of R, while counter-clockwise rotation (right) increases the already positive rotational strength. The Möbius-type coupling of the moments (see text) corresponds to the arrangement shown in the middle

the preceeding section. Calculated rotational strengths differ, though, mainly because of the modifications introduced. Like the simple MO picture PPP can account for the three experimentally observed absorptions (B, A$^+$, and B$^+$, respectively); note, however, that now the 300 and 240-nm band have rotational strengths of the same sign, again in contrast to the experiment.
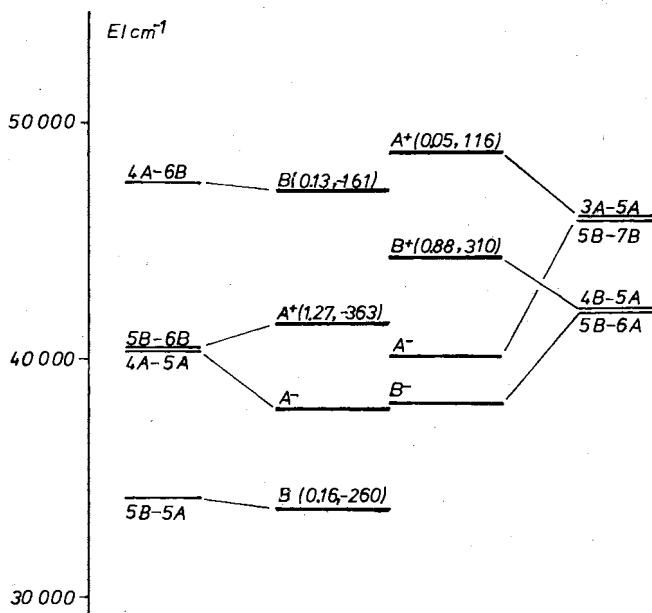

Figure 5. CI part of PPP calculation of M-chiral **1**. Numbering of orbitals is carried over from Figure 3. Values in parentheses behind state symbols correspond, respectively, to calculated oscillator and rotational strengths (in 10^{-40} cgs units)

CNDO Calculations

Results are bound to become more complicated in all-valence electron calculations due to extensive $\sigma\pi$ interaction in this highly twisted molecule. Surprisingly, the origin of most MOs can still be traced back to the simple MO picture developed in Figure 3, major differences being the interchange of MOs 4A and 4B and the stabilization of the group ii) states relative to those of group i) which results in an increase of interaction compared to PPP. Table 2 gives the results of all calculated spectral parameters; extension of the CI calculation by including doubly excited states does not improve the agreement with the experimental data.

The 300 nm Band. There can be little doubt about the nature of the longest-wavelength absorption, the HOMO − LUMO excitation in the absence of degeneracy being a rather pure state. All three calculations give the same general description of this state − long-axis polarized, B-type coupling of the transition moments with resulting little UV intensity. They differ in the sign of the rotational strength calculated for the state. The reason for this has been elucidated above. Choosing Möbius-type bonding in the PPP calculations may seem arbitrary. However, the agreement with the results of the CNDO calculations justifies this choice and lends additional support to the conclusions

reached. The effect of through-space interaction on the transition moments would go unnoticed from the UV spectrum alone, no theory being able to account for changes so subtle in oscillator strengths. At the same time it illustrates the sensitivity of CD data to minute structural and electronic details.

Tab. 2. Results of CNDO/S calculations on M-Triphenylenicene[a]

State	Energy [cm^{-1}]	Wavelength [nm]	f[b]	R[c] [10^{-40} cgs]
1 B$^+$	31625	316	.02	−96
1 B$^-$	32438	308	.01	−63
1 A$^-$	32842	304	−	−
1 A$^+$	34909	286	.07	17
2 A$^-$	38679	259	.24	96
2 B$^+$	39481	253	.52	151
2 A$^+$	41863	239	.67	−195
2 B$^-$	42575	235	.09	2
3 A$^+$	43863	228	.22	−36
3 B$^+$	44496	225	.25	−168

[a] CI based on 60 singlet excited states; geometry of **1** as in Figure 3. − [b] Oscillator strength. − [c] Rotational strength.

The 250 nm Band. According to CNDO/S the absorption around 250 nm is caused by two excitations, in both of which group ii) states participate, though to a different degree. The 2B$^+$ state is pure group ii), while in the other (A$^-$) there is strong coupling with the *cis* peak. The low-energy coupling of the two (2A$^-$) has the positive rotational strength of the A$^-$ part, while the high-energy combination (2A$^+$ at 239 nm) carries the negative sign of the *cis* peak and leads already to the next band.

The 225 nm Band. According to CNDO, three components including the just-mentioned 2A$^+$ state make up this band, all with negative strengths. 3B$^+$ corresponds to the positive combination of the 4A − 6B and 4B − 6A excitations, of which the latter, according to CNDO, comes into spectral range only because of destabilization of the degenerate 4B benzene MOs.

Conclusion

With its symmetry and pronounced inherent chirality it appears surprising at first that the interpretation of the CD spectrum of **1** should present such difficulty. The reason is the presence in the molecule of two elements of chirality at the same time, expressed, respectively, through the twist angles Θ and Φ, with, moreover, opposite senses of chirality. It seems, however, that following our analysis a strong case can be made for the origin of all three CD bands of **1**, mainly on the basis of the CNDO results.

The agreement between the CNDO-calculated signs of all three CD bands of M-helical triphenylenicene with the experimental data of (−)-**1** makes this assignment a plausible one. It does not agree with the absolute configuration assigned to **1** based on the similarity of its CD spectrum with that of a sulfur-containing cyclophane, **2**, whose structure was solved using Bijfoet's method[3].

Experimental

(+)- and (−)-**1** were a gift from Prof. Vögtle, Univ. of Bonn. — The CD spectra were obtained on a Jobin Yvon Dichrograph Mark IV with digital data accumulation, equipped for thermostatisized low-temperature measurements.

Computations: For molecular mechanics calculations Allinger's MMP2 force-field[14] was used. A standard PPP program was used; rotational strengths were calculated from the MO expansion and CI matrix in the dipole-velocity formalism, CNDO/S calculations were performed using the program CNDO which is part of the MONDO package[15].

CAS Registry Numbers

(−)-**1**: 84615-31-6

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4) There are different usages of this term. While some workers restrict it to molecules with at least a three-fold rotational axis or dihedral symmetry [M. Farina, C. Morandi, *Tetrahedron* **30** (1974) 1819], others call a structure "high symmetry chiral", if it contains at least one two-fold axis [M. Nakazaki, *Top. Stereochem.* **15** (1984) 199]. We prefer "symmetric chiral" for any molecule of at least C_2 symmetry as distinguished from "asymmetric chiral" for C_1 symmetry.
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