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Applications of MCD Spectroscopy: MO Ordering and Transannular Interaction in 1,6-Methano[10]annulenes from Analysis of Substituent Effects

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Abstract: Eight 2-substituted and nine 3-substituted 1,6-methano[10]annulenes have been synthesized, and their magnetic circular dichroism has been measured. The *B* terms of the L_b transition depend on the π-electron effect of the substituent in a way which reveals the ordering of the four frontier molecular orbitals: a_1, a_2, b_1, and b_2 in the order of increasing energy. This result implies the presence of a strong transannular interaction between the bridgehead positions 1 and 6 on the bridged [10]annulene ring.

Introduction

Methano-bridged medium-ring annulenes[2] (e.g., **1**) represent a group of stable aromatic compounds which represent useful models for the hypothetical planar annulenes of D_{nh} symmetry (e.g., **2**). The model is only approximate: the perturbation affecting the aromatic π system of **1** relative to **2** can be viewed as a superposition of (i) a geometrical distortion to lower symmetry, (ii) introduction of nonzero dihedral twist angles and deviations from parallelism of the axes of the "$2p_z$" atomic orbitals, (iii) introduction of an inductive effect at the bridgehead positions, (iv) introduction of a hyperconjugative effect of the CH_2 bridge, (v) introduction of direct transannular interaction between the "$2p_z$" AO's at the bridgehead atoms. In evaluating **1** as an approximate model for **2**, it is of interest to ask which of these five perturbing factors is dominant. The answer may well depend on the property used in the estimate of the degree to which **1** differs from **2**. Since the latter is only a hypothetical species, it is necessary to choose a property which can be safely predicted for **2** from theory alone. The ordering of the four frontier molecular orbitals, characterized by their nodal properties (Figure 1), is such a property, since they must be pairwise degenerate by symmetry in the hypothetical parent perimeter. It is also an important property since it is directly related to chemical reactivity. It needs to be recognized, of course, that the very concept of an orbital in a many-body system is only a part of an approximate model but so are the concepts of inductive effect, transannular interaction, etc. The following analysis will be based on the acceptance of the usual MO model of molecular structure as an adequate approximation to reality.

Initial studies of **1** by ultraviolet absorption[3] and photoelectron spectroscopy[4] led to the conclusion that the resonance integral between the "π" symmetry AO's on carbon atoms 1 and 6 was equal to nearly a half of that between neighbors in a planar perimeter. The presence of this interaction was also suggested[5] by an analysis of the bond length variation along the perimeter of **1**. Furthermore, the existence of an attractive transannular interaction between the two bridgehead carbon atoms in the ground state was deduced from a comparison of crystal structure data for a series of related compounds.[6] NMR spectra showed no unusual features, however, and a review article on homoaromaticity[7] expressed serious doubt that any transannular interaction is present in **1**. In a recent paper[8] the electronic spectra of **1** and its higher homologues with 14-electron and 18-electron perimeters were investigated and it was concluded that transannular interaction in these bridged annulenes indeed is important; it was pointed out that there is no contradiction with the NMR results.

In the present study, we have used magnetic circular dichroism (MCD) spectroscopy to determine the MO ordering in **1** and to obtain very direct evidence in favor of this conclusion. In permitting us to settle the particular problem of transannular interaction in methano-bridged annulenes, this provides an illus-

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[1] (a) University of Utah. (b) University of Cologne.

[2] Vogel, E. *Isr. J. Chem.* **1980**, *20*, 215; *Spec. Publ.—Chem. Soc.* **1967**, *No. 21*, 113.

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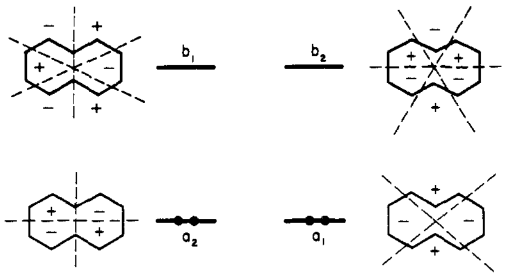


Figure 1. Nodal properties of the frontier orbitals of [10]annulene.

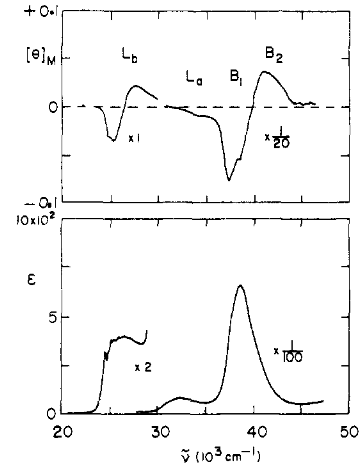


Figure 2. 2-Methyl-1,6-methano[10]annulene (2-Me-1) in cyclohexane: bottom, absorption; top, MCD (deg L mol^{-1} m^{-1} G^{-1}).

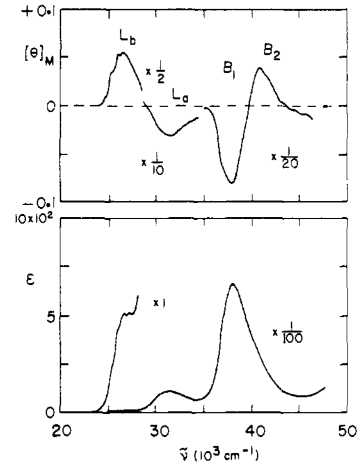


Figure 3. 2-Cyano-1,6-methano[10]annulene (2-CN-1) in cyclohexane: bottom, absorption; top, MCD (deg L mol^{-1} m^{-1} G^{-1}).

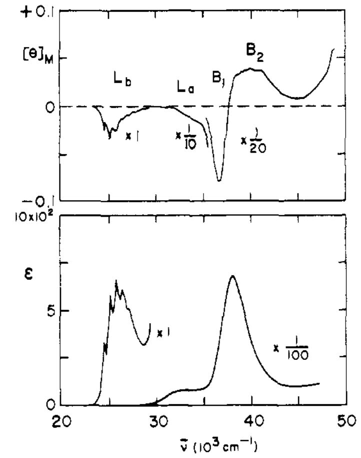


Figure 4. 3-Methoxy-1,6-methano[10]annulene (3-MeO-1) in cyclohexane: bottom, absorption; top, MCD (deg L mol^{-1} m^{-1} G^{-1}).

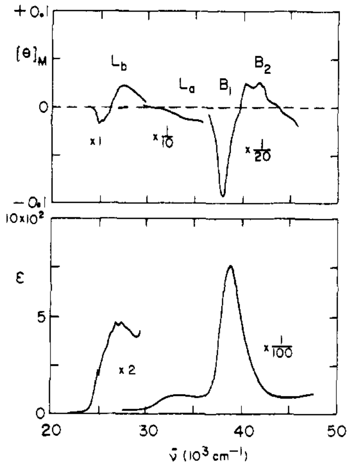


Figure 5. 3-Methyl-1,6-methano[10]annulene (3-Me-1) in cyclohexane: bottom, absorption; top, MCD (deg L mol^{-1} m^{-1} G^{-1}).

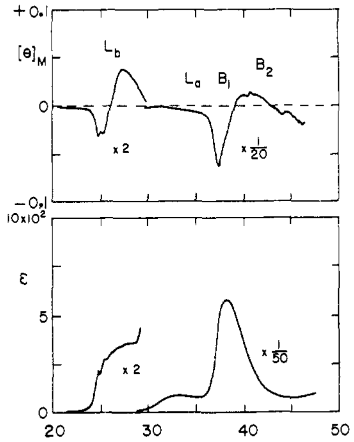


Figure 6. 3-(Trimethylsilyl)-1,6-methano[10]annulene (3-Me$_3$Si-1) in cyclohexane: bottom, absorption; top, MCD (deg L mol^{-1} m^{-1} G^{-1}).

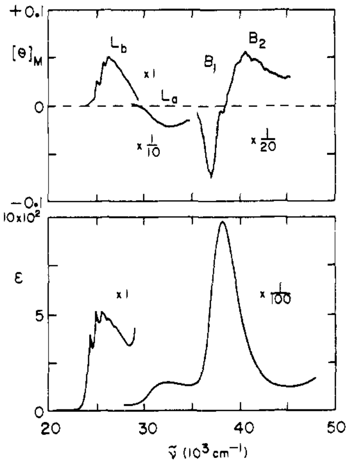
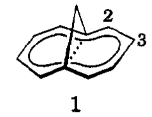


Figure 7. 3-Cyano-1,6-methano[10]annulene (3-CN-1) in cyclohexane: bottom, absorption; top, MCD (deg L mol^{-1} m^{-1} G^{-1}).

tration of the use of simple concepts of MCD spectroscopy in organic chemistry.



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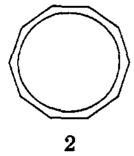

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Results and Discussion

Spectral Assignments. The spectra of all of the compounds investigated bear unmistakable similarity to those of the parent

Table I. *B* Terms of Substituted Derivatives of 1,6-Methano[10]annulene (1)[a]

substituent	position	L_b	L_a	B_1	B_2
none		−0.04	0.4	2.4	
$N(CH_3)_2$	2	0.89	−1.24	0.84	−0.48
OCH_3	2	0.49	−0.64	3.2	−2.2
Br	2	0.18	−0.42	2.54	−2.26
CH_3	2	0.01	0.42	2.8	−1.45
CN	2	−0.32	1.12	3.02	−1.15
COOH	2	−0.63	2.19	2.72	−0.62
$COOCH_3$	2	−0.56	2.28	1.54	−0.68
CHO	2	−0.70	2.3	2.2	−0.81
$N(CH_3)_2$	3	0.89	−0.59	2.39	−0.24
OCH_3	3	0.08	0.32	2.0	−2.47
Br	3	−0.06	0.45	1.53	−1.15
CH_3	3	−0.04	0.35	2.31	−0.83
$Si(CH_3)_3$	3	0.02	0.29	1.47	0.44
CN	3	−0.16	0.89	1.67	−2.5
COOH	3	−0.19	0.97	1.41	−0.54
$COOCH_3$	3	−0.14	0.48	1.31	−0.16
CHO	3	−0.32	1.23	3.27	−1.93

[a] *B* terms in units of $10^{-3}\ \beta_e\ D^2/cm^{-1}$.

1,6-methano[10]annulene (**1**).[8] Selected examples are shown in Figures 2–7. The spectra are dominated by four singlet-singlet transitions, interpretable in terms of Platt's perimeter model[9] as two weak *L* transitions at lower energies and two strong *B* transitions at higher energies. The high symmetry of parent **1** permits the assignment of its transitions as L_b, L_a, B_a, and B_b in the order of increasing energy,[3,8] where transitions with the subscript *b* are polarized along the long axis (horizontal in Figure 1) and those with the subscript *a* are polarized along the short axis. In the 2- and 3-substituted derivatives, this strict distinction is lost and all four states of the free perimeter can mix. The mixing is likely to be particularly strong for the two nearly degenerate *B* states. The observed intensity distributions indicate a much smaller degree of mixing for the *L* states. Consequently, we shall refer to the four transitions by the labels L_b, L_a, B_1, and B_2 in the order of increasing energy. In some cases, also a fifth transition, labeled *C* in ref 8, is clearly visible in the MCD spectrum, but its more detailed examination lies outside the scope of this paper.

The integrated MCD intensities (*B* terms) of **1** and its derivatives are collected in Table I. The accuracy of the values listed for the three higher energy transitions suffers from their mutual overlap but those for the quite well separated L_b transition should be reasonably accurate. If we assume that part of its integrated MCD intensity which is due to vibronic interactions with the higher energy transitions to be essentially constant throughout the series, we can use the simple perimeter model to interpret the observed trends and to deduce the sequence of the frontier molecular orbitals in the parent **1**. The details of the application of the model to molecules formally derived from $(4N + 2)$-electron conjugated perimeters can be found elsewhere,[10] as can a qualitative summary.[11]

Frontier Molecular Orbitals of 1. The nodal structure of the two highest bonding occupied MO's of **1** (a_1 and a_2) and of its two lowest antibonding unoccupied MO's (b_1 and b_2) follows from the fundamentals of the perimeter model (number of nodes) and from the C_{2v} symmetry of **1**. This structure is such that the a_1 and b_2 orbitals have a larger coefficient on perimeter atom 3 than on atom 2, while the a_2 and b_1 orbitals have a larger coefficient on atom 2 than on atom 3 (Figure 1).

In the hypothetical unperturbed D_{10h} 10π-electron [10]annulene **2**, the bonding MO's a_1 and a_2 would constitute a degenerate pair and so would the antibonding MO's b_1 and b_2. The degeneracy of the bonding MO pair is known to be split in the actual molecule **1** by about 0.5 eV, based on photoelectron spectra and Koopmans' theorem.[4] The proton coupling constants in the ESR spectrum of the radical anion of **1** show that the antibonding orbital pair is split as well and their magnitudes leave no doubt that the b_1 orbital lies below the b_2 orbital in energy; this was originally attributed to the inductive effect of the methano bridge.[12] The ESR spectrum of the radical cation has not been observed, and the order of the a_1, and a_2 orbital pair has not been established by experiment. It might be argued that strictly speaking, the photoelectron and ESR results depend on the properties of the radical ion states of **1** and are not a valid guide to the orbital structure of the parent **1**. While correct in principle, this objection is not of overriding concern for discussions within the framework for the usual MO model of chemical bonding. Still, it is of interest to establish the MO ordering using a method which depends on the states of the neutral **1** alone, as will be done in the following.

The various perturbations which are introduced by the 1,6-methano bridging which converts **2** to **1** have predictable effects on the energies of the four MO's of interest.

(i) Pure geometrical distortion of the perimeter changes the two-electron part of the Hamiltonian but does not affect primary bonding interactions in the perimeter. Its effect should be essentially negligible; PPP calculation suggests the order a_1, a_2, b_1, and b_2 in the order of increasing energy, with orbital energy splitting of ~0.05–0.1 eV for both pairs. This effect is clearly incapable of accounting for the observed splitting and will be ignored in the following.

(ii) Nonzero dihedral twist angles and deviations from parallelism of the axes of the "$2p_z$" AO's weaken the primary bonding interaction in **1** relative to **2**. Consideration of the experimental molecular geometry of a simple derivative[13] reveals that a fairly severe twisting (~35°) and weakening occurs for the perimeter π bonds originating at the bridgehead carbon atoms, while the rest of the perimeter is hardly affected. The reduction in these four resonance integrals will not affect the MO's a_2 and b_1 whose nodal plane passes through the bridgehead carbons. However, it will destabilize the MO a_1 (no node across the affected bonds) and stabilize the MO b_2 (node across the affected bonds), producing the orbital arrangement a_2, a_1, b_2, and b_1 in the order of increasing energy.

(iii) The electron-donating inductive effect of the CH_2 substituent will not affect the orbitals a_2 and b_1 to the first order, since they have a node through the bridgehead, and will destabilize the orbitals a_1 and b_1, leading to the orbital arrangement a_2, a_1, b_1, and b_2.

(iv) The electron-donating hyperconjugative effect of the methano bridge will be due to the interaction of the occupied out-of-phase combination of the two C–H σ-bond orbitals of the CH_2 group with the perimeter. This occupied hyperconjugating orbital has a nodal plane through the carbon atom of the CH_2 group and the two bridgehead carbon atoms, so that it is of b_1 symmetry and can interact only with the b_1 orbital of the perimeter. Thus, hyperconjugation cannot be responsible for the observed split of the a_1, a_2 MO pair. Moreover, this will be a weak interaction because of the large energy mismatch. Also, it will be counteracted by a similar weak interaction of the perimeter b_1 orbital with the unoccupied out-of-phase combination of the two C–H σ^*-antibond orbitals of the CH_2 group. All in all, hyperconjugation with the bridge is unlikely to have much effect on the orbital energies and should only produce a slight displacement of the b_1 orbital above b_2.

(v) Transannular interaction, i.e., direct through-space overlap of the "$2p_z$" orbitals on the two bridgehead carbons which form a part of the conjugated perimeter, will not affect the energies of the MO's a_2 and b_1, which have a nodal plane through the bridgehead carbon atoms. It will stabilize the MO a_1 (no node across the new resonance integral) and destabilize the MO b_2 (node across the new resonance integral). The anticipated orbital arrangement is a_1, a_2, b_1, and b_2 in the order of increasing energy.

Among the five perturbations, transannular interaction is unique in predicting the MO a_1 to lie significantly below a_2. Along with

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(9) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.

(10) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801, 6812, 6819.

(11) Michl, J. *Pure Appl. Chem.* **1980**, *52*, 1549.

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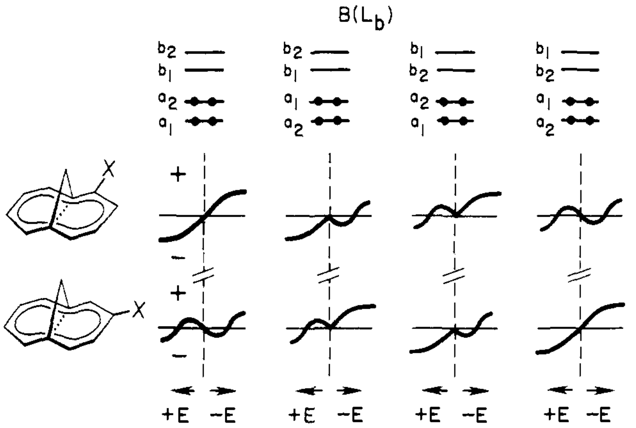

Figure 8. Perturbed [10]annulenes: theoretically expected dependence of B term of the L_b transition on substituent strength ($+E$, π acceptor; $-E$ π donor) for four possible arrangements of the four frontier orbitals.

the (negligible) effect of geometrical distortion and with the inductive effect, these are the only two perturbations which lead to the order b_1 below b_2 demanded by the ESR experiment on the radical anion of **1**. Clearly, if the orbital arrangement can be shown to be a_1, a_2, b_1, and b_2, the inescapable conclusion is that it is dictated by transannular interaction in spite of the other perturbations which are undoubtedly also present.

The *B* Terms of the L_b Transition. As discussed in detail elsewhere,[10,11] the sign and magnitude of the B terms of the L_b transition of a perturbed $(4N + 2)$-electron annulene are determined by two contributions. One of these is proportional to a small magnetic moment μ^-, is weakly positive for most perimeters (including the 10-electron [10]annulene perimeter), and is very insensitive to structural perturbations. The other is proportional to a large magnetic moment μ^+ and is highly sensitive to molecular structure. When the energy difference of the two highest energy occupied perimeter MO's, ΔHOMO, is equal to that of the two lowest energy empty perimeter MO's, ΔLUMO, the μ^+ contribution vanishes. Simple PPP theory predicts this to be the case for **1** since it is an alternant hydrocarbon as long as the inductive and hyperconjugative effects of the bridge are ignored (above factors iii and iv). When ΔHOMO > ΔLUMO, the μ^+ contribution to the B term is predicted to be positive, and when ΔHOMO < ΔLUMO, it is predicted to be negative. Experimentally, the B term of the L_b transition of **1** is almost exactly zero, and we take this to mean that its weakly positive μ^- contribution is nearly exactly cancelled by the effects of a slight deviation from perfect pairing symmetry which cause the difference of the energies of orbitals a_1 and a_2, ΔHOMO, to be slightly smaller than that of orbitals b_1 and b_2, ΔLUMO, and thus produce a weakly negative μ^+ contribution. The way in which the existence of two opposing contributions produces a bisignate MCD band for the L_b transition in **1** has already been discussed elsewhere.[8] The details of this nearly perfect cancellation are immaterial for the following argument in which only differences in integrated MCD intensities (B terms) between **1** and its substituted derivatives are considered, and these will depend nearly exclusively on changes in the μ^+ contribution.

For each possible orbital ordering, the effect of substitution on the relative size of ΔHOMO and ΔLUMO is predicted readily by PMO theory, relying on the knowledge of the relative sizes of the MO coefficients in positions 2 and 3. Using the signs and magnitudes of the B term of the L_b transition in monosubstituted benzenes[14] as a measure of the net electron-withdrawing ($+E$) or electron-donating ($-E$) mesomeric effect of a substituent and plotting this quantity horizontally, we show in Figure 8 the anticipated plot of the B term of the L_b transition of the perturbed annulene **1** for each possible orbital arrangement as a function of substituent strength for both positions of substitution. Previous work on substituted naphthalenes indicated clearly that the inductive effect of the substituents is of subordinate importance (e.g., fluorine behaves as a donor).[15]

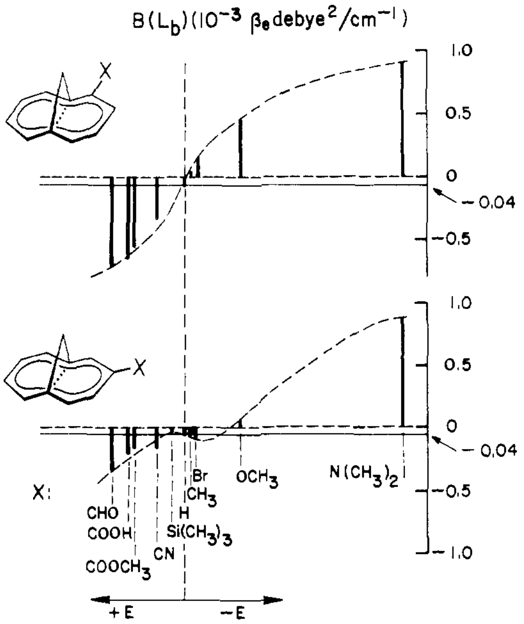

Figure 9. Perturbed [10]annulenes: the observed dependence of the B terms of the L_b transition (plotted vertical) on substituent strength (plotted horizontal). The B terms of the L_b transition of monosubstituted benzenes were used a measure of the π-electron strength of the substituents. The solid horizontal lines indicate the B term of the L_b transition of the parent **1**.

For instance, to predict the dependence of the B term of the L_b transition for **1** with a $+E$ substituent in position 2, one recognizes that the empty acceptor orbital of the substituent will interact more strongly with the MO b_1 than with b_2 which has a much smaller coefficient in this position and that it will interact much more weakly with orbitals a_1 and a_2 which are far away in energy. Thus, if b_2 lies above b_1, the $+E$ substituent in position 2 will increase ΔLUMO, leaving ΔHOMO almost unchanged, so that a negative μ^+ contribution to the B term is predicted. On the other hand, if b_1 lies above b_2, the $+E$ substituent in position 2 will reduce ΔLUMO, leaving ΔHOMO almost unchanged, so that a positive μ^+ contribution to the B term is predicted. In the latter case, as the $+E$ effect of the substituent increases in strength, it will eventually push the b_1 orbital below b_2 and then make ΔLUMO equal to ΔHOMO. At that point, a vanishing μ^+ contribution to the B term is predicted. For even stronger $+E$ substituents, ΔLUMO will exceed ΔHOMO and a negative μ^+ contribution to the B term must be expected. Such a sign reversal of a B term with increasing strength of a substituent located in what has been called a subdominant position[10,11] has been observed in cases where it is predicted by theory.[15,16]

Predictions for substitution in position 3 are based on the recognition of the fact that b_2 now has a larger coefficient than b_1. Predictions for $-E$ substituents are based on their effect on the orbitals a_1 and a_2, which will now be far larger than that on the orbitals b_1 and b_2.

A comparison with the plot of the experimental results (Figure 9) leaves absolutely no doubt that the orbital arrangement in **1** must be a_1, a_2, b_1, and b_2 in the order of increasing energy. As discussed above, this implies that the orbital ordering is dictated by the effects of transannular interaction.

Since this study represents the first use of MCD spectroscopy for the purpose of establishing the MO sequence in an aromatic perimeter, we have put considerable effort into performing the

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(14) Shieh, D. J.; Lin, S. H.; Eyring, H. *J. Phys. Chem.* **1973**, *77*, 1031. Kaito, A.; Tajiri, A.; Hatano, M. *J. Am. Chem. Soc.* **1976**, *98*, 384.

(15) Whipple, M. R.; Vasak, M.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6844.

(16) Wallace, S. L.; Castellan, A.; Muller, D.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6828.

measurements on a large enough number of derivatives of **1** to permit the tracing of the full curves shown in Figure 9. This represents considerable overkill and in future studies of this kind only the use of a few judiciously chosen substituents will be called for.

Finally, it remains to be noted that the sequence a_1, a_2, b_1, and b_2 agrees with the results of ab initio calculations[17] and with the arguments presented in the early work on the electronic structures of **1**.[3,4] The order a_1 and a_2 is in agreement with the known[2] reactivity pattern in electrophilic substitution on **1**, which proceeds faster in position 2 than in position 3. We believe that the presence of the a_1, a_2, b_1, and b_2 orbital ordering also definitively settles the question of the presence of significant transannular interactions in **1** in the affirmative sense.

Experimental Section

Synthesis. General Data. Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 infrared spectrometer as films or as KBr pellets. Ultraviolet spectra were obtained with a Beckman Model 25 spectrometer. Nuclear magnetic resonance spectra were determined on a Varian EM 390 spectrometer (90 MHz). Chemical shifts are reported in δ values from an internal standard of tetramethylsilane. Low-resolution mass spectra were obtained on a Finnigan 3200 mass spectrometer (70 eV) and high-resolution mass spectra were determined on a Varian MAT 212 mass spectrometer. For column chromatography, Macherey-Nagel & Co. silica gel (particle size 0.063–0.2 mm, 70–230 mesh) or Woelm alumina (act. II–III acc. to Brockmann) were used.

1-Formyl-6-vinylcyclohepta-1,3,5-triene (3). Triphenylmethylphosphonium bromide (39.2 g, 0.11 mol) and sodium bis(trimethylsilyl)amide (20.13 g, 0.11 mol) were dissolved in 400 mL of dry THF and heated at reflux for 0.5 h under an argon atmosphere. The solution was filtered through an inert gas frit directly into a dropping funnel and then added dropwise over 1.5 h to a solution of 1,6-diformylcyclohepta-1,3,5-triene[18] (14.8 g, 0.1 mol) in 1.2 L of dry THF at 0.5 °C under argon. The cooling bath was removed and the reaction mixture stirred for 2 h. After the mixture was heated at reflux for 0.25 h, the solvent was removed in vacuo at room temperature, the residue taken up in dichloromethane, and the solution filtered through silica gel. The chromatography of the product on silica gel with dichloromethane–hexane (1:1) afforded a pale yellow oil of the divinyl compound (3.1 g, 22%) as the first fraction. The second fraction was the title compound **3** (5.9 g, 40%) obtained as a bright yellow oil. Final elution with dichloromethane and recrystallization of the crude product from ethyl acetate yielded 2.8 g (19%) of unreacted starting material. The 1-formyl-6-vinylcyclohepta-1,3,5-triene (**3**) obtained was pure enough for the further reaction. An analytical sample was prepared by distillation: bp 60 °C (0.2 torr); IR (neat) 3003, 2805, 2710, 1662 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 9.56 (s, 1 H), 7.03–6.2 (m, 5 H), 5.93 (d, 1 H), 5.25 (d, 1 H), 2.78 (s, 2 H); mass spectrum, M$^+$ at *m/e* 146. Anal. Calcd for the oxime ($C_{10}H_{11}NO$): C, 74.53; H, 6.83; N, 8.70. Found: C, 74.60, H, 6.88; N, 8.79.

1-(2,2-Dibromovinyl)-6-vinylcyclohepta-1,3,5-triene (4). Carbon tetrabomide (16.6 g, 50 mmol) and triphenylphosphine (28.8 g, 110 mmol) were dissolved in 300 mL of dry dichloromethane at 0 °C under an argon atmosphere. After the orange solution was stirred for 15 min, 1-formyl-6-vinycyclohepta-1,3,5-triene (**3**, 5.84 g, 40 mmol) was added quickly. This reaction mixture was stirred for 30 min at room temperature. Fifty milliliters of water was added, and the organic layer was washed with water twice. After the solution was dried and the solvent removed, the product was chromatographed on silica gel with dichloromethane–hexane to yield 10.6 g (88%) of the pure compound **4** as a yellow, thermally unstable, air-sensitive oil: IR (neat) 3012, 2899, 2844, 1615, 1583, 1564 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 6.93 (s, 1 H), 6.6–6.03 (m, 5 H), 5.43 (d, 1 H), 5.15 (d, 1 H), 2.65 (s, 2 H); UV (cyclohexane) 332 (ϵ 7520), 255 nm (25 800); mass spectrum, M$^+$ at *m/e* 302. Exact Mass calcd for $C_{11}H_{10}Br_2$: 301.9130. Found: 301.9126.

3-Bromo-1,6-methano[10]annulene (3-Br-1). 1-(2,2-Dibromovinyl)-6-vinylcyclohepta-1,3,5-triene (**4**, 10.57 g, 35 mmol) was dissolved in 150 mL of dry dimethylformamide and heated at reflux for 0.5 h under an argon atmosphere. The reaction mixture was cooled to room temperature, poured into 250 mL of water, and extracted with hexane. The organic phase was washed with water and dried over magnesium sulfate. After removal of the solvent, the distillation of the residue gave 6.7 g (86%) of 3-bromo-1,6-methano[10]annulene (**3-Br-1**) as yellow liquid: bp 93–94 °C (0.05 torr); IR (neat) 3030, 2945, 1573 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.6 (s, 1 H), 7.4–6.9 (m, 6 H), –0.4 (s, 2 H); UV (cyclohexane) 406 (ϵ 76), 400 (93, sh), 392 (137, sh), 383 (198), 375 (230), 367 (241), 305 (6540), 265 nm (61 000); mass spectrum, M$^+$ at *m/e* 220/222. Anal. Calcd for $C_{11}H_9Br$: C, 59.75; H, 4.10; Br, 36.14. Found: C, 59.54; H, 4.10, Br, 36.04.

2-Bromo-1,6-methano[10]annulene (2-Br-1) was prepared by a published procedure.[19,20]

3-Methoxy-1,6-methano[10]annulene (3-MeO-1). Sodium (575 mg, 25.0 mmol) was dissolved in 6 mL of dry methanol under an argon atmosphere, and the solution was diluted with 15 mL of dry hexamethylphosphoric triamide (HMPA). 3-Bromo-1,6-methano[10]annulene (**3-Br-1**, 1.105 g, 5.0 mmol) in 15 mL of dry HMPA was added and the mixture stirred for 2 h at 80 °C. A saturated solution of nickel chloride in water was added, the mixture extracted with ether, and the ether phase washed with water. After the solution was dried the solvent removed in vacuo, the residue was filtered with ether–hexane (1:2) through silica gel. The product recovered was recrystallized from hexane to yield 670 mg (78%) of the pale yellow needles: mp 64 °C; IR (KBr) 3033, 2924, 1575, 1538, 1260, 1156 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.53–6.76 (m, 7 H), 4.0 (s, 3 H), –0.3 (AB system, J = 9 Hz, 2 H); UV (dioxane) 406 (ϵ 386), 396 (705), 387 (820), 378 (772), 371 (664, sh), 301 (6370), 264 nm (59 000); mass spectrum, M$^+$ at *m/e* 172. Exact Mass Calcd for $C_{12}H_{12}$: 172.0888. Found: 172.0885.

2-Methoxy-1,6-methano[10]annulene (2-MeO-1). The aforementioned procedure applied to 2-bromo-1,6-methano[10]annulene (**2-Br-1**, 1.105 g, 5.0 mmol) afforded 740 mg (86%) of a yellow oil: bp 87 °C (0.2 torr); IR (neat) 3036, 2998, 2943, 1492, 1244 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.7–6.75 (m, 6 H), 6.3 (d, 1 H), 3.9 (s, 3 H), –0.03 (d, 1 H), –0.83 (d, 1 H); UV (cyclohexane) 410 (ϵ 795, sh), 403 (845), 318 (5950), 265 (34 900, sh), 255 nm (43 100); mass spectrum, M$^+$ at *m/e* 172. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02; Found: C, 83.97; H, 6.67. See also ref 21.

3-(Dimethylamino)-1,6-methano[10]annulene (3-Me$_2$N-1). A solution of *n*-butyllithium (30 mL, 1 M in ether) was added to 20 mL of condensed dimethylamine at –20 °C under argon and stirred for 0.5 h. Forty milliliters of dry hexamethylphosphoric triamide (HMPA) was added to dissolve the precipitated salt. 3-Bromo-1,6-methano[10]annulene (**3-Br-1**, 2.21 g, 10 mmol) in 20 mL of HMPA was quickly added at –40 °C, and the mixture was stirred for 15 min. The reaction mixture was first hydrolyzed with methanol and then with water and diluted with water and ether, and the aqueous layer was extracted with ether. The combined ether layers were washed with water and dried over sodium sulfate. After the solvent was removed in vacuo, the product was chromatographed through neutral alumina with pentane to yield a yellow liquid. Distillation afforded 1.4 g (76%) of an air-sensitive yellow oil: bp 92 °C (0.1 torr); IR (neat) 3030, 2942, 2868, 2795, 1581, 1545 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.36–6.36 (m, 7 H), 3.03 (s, 6 H), –0.32 (AB system, J = 9 Hz, 2 H); UV (dioxane) 408 (ϵ 2760), 342 (10 700), 282 (38 100), 246 nm (21 500); mass spectrum, M$^+$ at *m/e* 185. Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; 7.56. Found: C, 83.87; H, 8.12; N, 7.51.

2-(Dimethylamino)-1,6-methano[10]annulene (2-Me$_2$N-1). The aforementioned procedure was applied to 2-bromo-1,6-methano[10]annulene (**2-Br-1**, 2.21 g, 10 mmol) except that the lithium amide solution was dropped into a solution of 2-bromo-1,6-methano[10]annulene in ether–HMPA. There was obtained 530 mg (29%) of the product as a yellow, air-sensitive oil: bp 94 °C (0.1 torr); IR (neat) 2942, 2868, 2838, 2788, 1503 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.43–6.57 (m, 6 H), 5.97 (d, 1 H), 3.2 (s, 6 H), 0.25 (d, 1 H), –0.75 (d, 1 H); UV (cyclohexane 405 (ϵ 2210, sh), 351 (11 300), 271 (28 500, sh), 251 nm (42 200); mass spectrum, M$^+$ at *m/e* 185. Exact Mass Calcd for $C_{13}H_{15}N$: 185.1204. Found: 185.1210.

3-(Trimethylsilyl)-1,6-methano[10]annulene (3-Me$_3$Si-1). 3-Bromo-1,6-methano[10]annulene (**3-Br-1**, 663 mg, 3 mmol) was dissolved in 60 mL of dry THF and 20 mL of dry pentane. A solution of *n*-butyllithium (3 mL, 1 M in hexane) was added at –100 °C over 5 min under an argon atmosphere and stirred for 20 min. One milliliter of trimethylsilyl chloride was added, and the reaction mixture was allowed to warm to room temperature. After the solvent was removed in vacuo, the residue was chromatographed on neutral alumina with hexane. Further purification by preparative GC (OV 101–180 °C) and then distillation afforded 340 mg (53%) of 3-(trimethylsilyl)-1,6-methano[10]annulene

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(3-Me_3Si-**1**): bp 97 °C, 0.3 torr; IR (neat) 3041, 2955, 2900, 1251, 1041, 836 cm^{-1}; ^1H NMR (CCl_4) δ 7.04–7.56 (m, 7 H), 0.39 (s, 9 H), −0.4 (s, 2 H); UV (cyclohexane) 402 (ϵ 128), 391 (165, sh), 386 (171, sh), 378 (192, sh), 369 (209, sh), 356 (220, sh), 299 (6650), 261 nm (6800); mass spectrum, M^+ at *m/e* 214. Exact Mass Calcd for $C_{14}H_{18}Si$: 214.1177. Found: 214.1185.

3-Cyano-1,6-methano[10]annulene (3-CN-1). 3-Bromo-1,6-methano[10]annulene (3-Br-**1**, 6.63 g, 30 mmol) and cuprous cyanide (10.74 g, 120 mmol) were heated in 100 mL of dry dimethylformamide for 2 h at reflux. The reaction mixture was cooled to room temperature, poured into a solution of 40 g anhydrous $FeCl_3$ in 40 mL of concentrated hydrochloric acid and 200 mL water, and stirred for 20 min at 70 °C. This mixture was extracted with dichloromethane and the organic phase washed with water. After the solution was dried and the solvents were removed in vacuo, the residue was chromatographed on silica gel with dichloromethane–hexane (1:1) as eluting solvent. Recrystallization of the product from hexane–ethyl acetate (2:1) afforded 4.2 g (84%) of pure 3-cyano-1,6-methano[10]annulene (3-CN-**1**) as pale yellow crystals: mp 62–63 °C; IR (KBr) 3051, 2948, 2211 cm^{-1}; ^1H NMR (CCl_4) δ 7.83 (s, 1 H), 7.68–7.16 (m, 6 H), −0.3 (AB system, J = 9 Hz, 2 H); UV (dioxane) 408 (ϵ 355), 398 (497), 388 (502), 378 (465), 370 (418, sh), 362 (361, sh) 311 (8110), 263 nm (67 200); mass spectrum, M^+ at *m/e* 167. Anal. Calcd for $C_{12}H_9N$: C, 86.2; H, 5.43; N, 8.38. Found: C, 86.15; H, 5.46; N, 8.40.

2-Cyano-1,6-methano[10]annulene (2-CN-1). The aforementioned procedure applied to 2-bromo-1,6-methano[10]annulene (2-Br-**1**, 6.63 g, 30 mmol) afforded 4.4 g (88%) of a yellow oil: bp 115 °C (0.2 torr); IR (neat) 3041, 2948, 2212 cm^{-1}; ^1H NMR (CCl_4) δ 7.9–7.1 (m, 7 H), −0.4 (AB system, J = 9 Hz, 2 H); UV (dioxane) 395 (334, sh) 381 (572, sh), 370 (685, sh), 362 (725, sh), 326 (7700), 265 nm (48 900); mass spectrum, M^+ at *m/e* 167. Exact Mass Calcd for $C_{12}H_9N$: 167.0734. Found: 167.0733.

3-Formyl-1,6-methano[10]annulene (3-CHO-1). To an ice-cooled, stirred solution of 3-cyano-1,6-methano[10]annulene (3-CN-**1**, 3.34 g, 20 mmol) in 100 mL of dry toluene was added dropwise 20 mL (24 mmol) of DIBAH in toluene. The reaction mixture was stirred for 0.5 h at room temperature. After acid hydrolysis and extraction with either the organic layer was washed with water and dried. Distillation of the residue gave 2.05 (60%) of the pure aldehyde as a yellow oil: bp 117–119 °C (0.05 torr). All physical properties were in accord with those reported.[22]

2-Formyl-1,6-methano[10]annulene (2-CHO-1) was prepared according to ref 20.

3-Methyl-1,6-methano[10]annulene (3-Me-1). 3-Formyl-1,6-methano[10]annulene (3-CHO-**1**, 1.7 g, 10 mmol) was added to a solution of potassium hydroxide (5.0 g) and 85% hydrazine hydrate (2.5 g) in 30 mL of triethylene glycol. The mixture was heated to 180 °C with stirring for 2 h, and water and some product were distilled off. The cooled reaction mixture was added to the distillate, poured into 200 mL of ice water, and extracted with pentane. The pentane phase was washed with water and dried. After removal of the solvent in vacuo, the residue was distilled to yield 1.3 g (83%) of 3-methyl-1,6-methano[10]annulene (3-Me-**1**) as a pale yellow oil: bp 73 °C (0.2 torr); IR (neat) 3042, 2950, 2870, 1920 (w), 1837 (w), 1790 (w), 1745 (w), 1705 (w) cm^{-1}; ^1H NMR (CCl_4) δ 7.4–6.8 (m, 7 H), 2.52 (s, 3 H), −0.46 (AB system, J = 9 Hz, 2 H); UV (cyclohexane) 403 (ϵ 101), 380 (189), 372 (213), 364 (214), 375 (202), 299 (6200), 260 nm (66 700); mass spectrum, M^+ at *m/e* 156. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.55.

2-Methyl-1,6-methano[10]annulene (2-Me-1). The aforementioned procedure applied to 2-formyl-1,6-methano[10]annulene (2-CHO-**1**, 1.7 g, 10 mmol) yielded 1.35 g (86%) of 2-methyl-1,6-methano[10]annulene (2-Me-**1**) as a pale yellow oil: bp 60 °C (0.03 torr); IR (neat) 3050, 2960, 1930, 1730, 1450 cm^{-1}, ^1H NMR (CCl_4) δ 7.5–6.76 (m, 7 H), 2.56 (s, 3 H), −00.5 (AB system, J = 9 Hz, 2 H); UV (cyclohexane) 407 (ϵ 145), 399 (149, sh), 396 (174), 391 (175), 382 (179), 374 (182), 366 (177), 357 (163, sh), 309 (6500), 259 nm (60 500); mass spectrum, M^+ at *m/e* 156. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.74. See also ref 20.

1,6-Methano[10]annulene-3-carboxylic Acid (3-COOH-1). A solution of sodium hydroxide (1.0 g, 25 mmol) in 25 mL of water was added to a stirred solution of silver nitrate (1.87 g, 11.0 mmol) in 25 mL of water. To this suspension of silver oxide was added a solution of 3-formyl-1,6-methano[10]annulene (3-CHO-**1**, 850 mg, 5 mmol) in 5 mL of methanol and stirred for 2 h at room temperature. The precipitate was separated by vacuum filtration and washed with 5% sodium hydroxide solution. The aqueous phase was washed with dichloromethane, acidified with dilute hydrochloric acid, and extracted with dichloromethane. The organic phase was washed with water and dried, and the solvent removed in vacuo. Two recrystallizations from ethyl acetate afforded 680 mg (73%) of the analytically pure carboxylic acid 3-COOH-**1**, as pale yellow crystals; mp 148–149 °C. All physical properties agreed with those reported.[21]

1,6-Methano[10]annulene-2-carboxylic acid (2-COOH-1) was prepared by a published procedure.[20,23]

3-Carbomethoxy-1,6-methano[10]annulene (3-COOMe-1). 3-Formyl-1,6-methano[10]annulene (3-CHO-**1**, 850 mg, 5 mmol) was added to a suspension of sodium cyanide (1.47 g), glacial acetic acid (530 mg), and active manganese dioxide (10 g) in 100 mL of absolute methanol. The mixture was stirred for 5 h at room temperature and filtered and the solvent removed in vacuo. The residue was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent, chromatogrphy of the residue on silica gel with ether–pentane (1:2), and crystallization from hexane gave 810 mg (81%) of the pure ester (3-COOMe-**1**) as pale yellow crystals; mp 36–37 °C. All physical properties were in accord with those reported.[22]

2-Carbomethoxy-1,6-methano[10]annulene (2-COOMe-1). The aforementioned procedure applied to 2-formyl-1,6-methano[10]annulene (2-CHO-**1**, 850 mg, 5 mmol) yielded 840 mg (84%) of the desired ester 2-COOMe-1: mp 40–41 °C; IR (neat) 3050, 2960, 1710, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 8.4–7.1 (m, 7 H), 3.95 (s, 3 H), −0.5 (s, 2 H); UV (cyclohexane) 406 (ϵ 179, sh), 398 (477, sh), 383 (750, sh), 377 (815), 328 (8150), 267 nm (38 800); mass spectrum, M^+ at *m/e* 200. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.87; H, 6.10.

Measurements. Spectra were measured in spectral grade cyclohexane. Absorption was recorded on a Cary 17 spectrophotometer and magnetic circular dichroism on a JASCO 500 C spectropolarimeter equipped with a 15-kG electromagnet. The CD measurement was calibrated against *d*-camphorsulfonic acid and tris(ethylenediamine)cobalt(III) iodide according to ref 24. The MCD measurement was calibrated against naphthalene[25,26] and cobalt(II) sulfate.[27] The B terms were evaluated from the formula $B = -33.53^{-1}\int d\tilde{\nu}\ [\theta]_M/\tilde{\nu}$, where $\tilde{\nu}$ is wavenumber $[\theta]_M$ is molar ellipticity per unit magnetic field in deg L m^{-1} mol^{-1} G^{-1}.

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Note Added in Proof. A reviewer has found it essential that the presence of significant transannular interaction be indicated in formula **1** by drawing a dotted line across the ring. We consider this is a formality since in many molecules whose properties are affected by transannular interaction such lines are not explicitly shown in the customary representation, yet they are understood (e.g., in *p*-cyclophane). To indicate that the transannular resonance integral is only less than half of those along the perimeter, we show a dotted line across the ring and a full circle along the perimeter. To a first approximation, the π system is that of [10]annulene; a more descriptive term is homonaphthalene.

Registry No. 1, 2443-46-1; 2-Me_2N-**1**, 85283-05-2; 2-MeO-**1**, 58853-55-7; 2-Br-**1**, 15825-92-0; 2-Me-**1**, 58790-01-5; 2-CN-**1**, 54004-10-3; 2-COOH-**1**, 5873-56-3; 2-COOMe-**1**, 58790-02-6; 2-CHO-**1**, 40563-42-6; 3-Me_2N-**1**, 85283-06-3; 3-MeO-**1**, 83845-00-5; 3-Br-**1**, 83845-01-6; 3-Me-**1**, 53146-88-6; 3-$(CH_3)_3Si$-**1**, 85283-07-4; 3-CN-**1**, 56220-99-6; 3-COOH-**1**, 53883-23-1; 3-COOMe-**1**, 53883-24-2; 3-CHO-**1**, 53883-22-0; **3**, 68050-88-4; **3** oxime, 85283-09-6; **4**, 85283-08-5; triphenylmethylphosphonium bromide, 1779-49-3; sodium bis(trimethylsilyl)amide, 1070-89-9; 1,6-diformylcyclohepta-1,3,5-triene, 28172-94-3; 1,6-divinylcyclohepta-1,3,5-triene, 50785-96-1.

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