JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

© Copyright 1984 by the American Chemical Society

VOLUME 106, NUMBER 9 MAY 2, 1984

Models for π–π Interactions in "Molecular Metals". Ionization Energies, Electronic Structure, and Through-Space/Through-Bond Interactions in [2.2]Paracyclophane. A Hartree–Fock–Slater Study

Kathleen A. Doris, Donald E. Ellis,* Mark A. Ratner,* and Tobin J. Marks*

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received July 5, 1983*

Abstract: This contribution reports a detailed study of the interactions involving the two cofacial π-electron systems in [2.2]paracyclophane, using the first principles discrete variational method local exchange (DV-Xα) technique. Excellent agreement with experimental PES-derived orbital energies and orderings is obtained. Through studies of carefully selected component model structures (cofacial benzene molecules, cofacial bent benzene molecules, *p*-xylene, bent *p*-xylene) it is possible to partition "through-space" (π–π) and "through-bond" (π–σ–π) interactions. The former interaction (ca. 1.3 eV) is larger than the latter and is also studied as a function of interplanar spacing; it is expected to be dominant in π-based molecular conductors. The through-bond interaction, which decreases the through-space splitting of one pair of occupied π levels, consists of two components. The highest occupied π level mixes with an unoccupied bridge orbital and is lowered in energy by 0.8 eV; the third highest occupied π level mixes with an occupied bridge level and is raised in energy by 0.2 eV. Thus, the total through-bond effect on the through-space splitting is ca. 1.0 eV, larger than previous studies have indicated. The importance of the separation of functional group interactions to studies of the bandwidths of organic metals is stressed as is the relevance of the through-space interaction to the understanding of molecular chain conductors.

The nature and magnitude of the interactions between the π-electron systems of cofacially arrayed molecular components are of crucial importance is understanding the collective properties of low-dimensional molecular materials.[1] Consequently, considerable experimental and theoretical effort has been directed at this problem.[1] While experimental studies have necessarily focused upon complex, in situ multimolecular properties, many of the theoretical investigations have approached these interactions from conceptually and computationally more tractable model systems, such as hypothetical dimers.[2] To bridge this gap, it would clearly be desirable to have available for study low molecular weight fragments of "molecular metal" lattices which could be jointly characterized by small molecule spectroscopic (e.g., high-resolution, He-I,II gas-phase PES) and quantum mechanical (e.g., discrete variational method local exchange (DV-Xα)[3]—vide infra) techniques. Such an experimental/theoretical effort is under way in this Laboratory,[4] using "capped" group 4A phthalocyaninato dimers and trimers[4,5] (A, B) to understand the properties of electrically conductive, cofacially arrayed phthalocyanine polymers C.[6]

---

(1) (a) Miller, J. S., Ed. "Extended Linear Chain Compounds"; Plenum Press: New York, 1982; Vols. 1–3. (b) Epstein, A. J., Conwell, E. M., Eds. "Proceedings of the International Conference on Low-Dimensional Conductors"; Boulder, CO, Aug 9–14, 1981; *Mol. Cryst. Liq. Cryst.* **1981–1982**, Parts A-F. (c) Alcâcer, L., Ed. "The Physics and Chemistry of Low-Dimensional Solids"; Reidel: Dordrecht, Holland, 1980. (d) Devreese, J. T., Evrard, R. P., van Doren, V. E., Eds. "Highly Conducting One-Dimensional Solids"; Plenum Press: New York, 1979. (e) Hatfield, W. E., Ed. "Molecular Metals"; Plenum Press: New York, 1979.

(2) (a) Grant, P. M. *Phys. Rev. B* **1983**, *27*, 3934–3947; (b) *Ibid.* **1982**, *26*, 6888–6895 and references therein. (c) Herman, F. *Phys. Scr.* **1977**, *16*, 303–306. (d) Herman, F.; Salahub, D. R.; Messmer, R. P. *Phys. Rev. B* **1977**, *16*, 2453–2465.

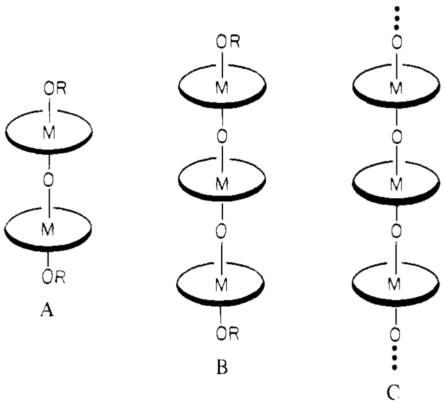
(3) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41–51. (b) Berkovitch-Yellin, Z.; Ellis, D. E.; Ratner, M. A. *Ibid.* **1981**, *62*, 21–35. (c) Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949–1960. (d) Rosen, A.; Ellis, D. E.; Adachi, H.; Averill, F. W. *Ibid.* **1975**, *65*, 3629–3634. (e) Ondrechen, M. J.; Ratner, M. A.; Ellis, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 1656–1659.

(4) (a) Doris, K. A.; Ratner, M. A.; Marks, T. J. Midwest Theoretical Chemistry Conference, 1982. (b) Doris, K. A.; Ratner, M. A.; Ellis, D. E.; Delley, B.; Marks, T. J. *Bull. Am. Phys. Soc.* **1983**, *28*, 245. (c) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragalâ, I. F.; Herbstein, F. H.; Ratner, M. A.; Marks, T. J., submitted for publication.

(5) (a) Hush, N. S.; Cheung, A. S. *Chem. Phys. Lett.* **1977**, *47*, 1–4. (b) Hush, N. S.; Woolsey, I. S. *Mol. Phys.* **1971**, *21*, 465–474.

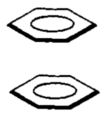
(6) (a) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551–1567. (b) Dirk, C. W.; Inabe, T.; Schoch, K. F., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539–1550. (c) Dirk, C. W.; Inabe, C. W.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Polym. Sci., Polym. Symp.* **1983**, *70*, 1–29. (d) Inabe, T.; Lyding, J. W.; Moguel, M. K.; Marks, T. J. *J. Phys.* **1983**, *C3*, 625–631. (e) Dirk, C. W.; Schoch, K. F., Jr.; Marks, T. J. In "Conductive Polymers"; Seymour, R. B., Ed.; Plenum Press: New York, 1981; Polymer Science and Technology Series, Vol. 15, pp 209–226. (f) Dirk, C. W.; Mintz, E. A.; Schoch, K. F., Jr.; Marks, T. J. *J. Macromol. Sci., Chem.* **1981**, *A16*, 275–298. (g) Marks, T. J.; Schoch, K. F., Jr.; Kundalkar, B. R. *Synth. Met.* **1980**, *1*, 337–347. (h) Schoch, K. F., Jr.; Kundalkar, B. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7071–7073.

0002-7863/84/1506-2491$01.50/0 © 1984 American Chemical Society

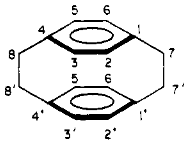


M = Si, Ge, Sn; R = capping functionality

As a prelude to and a calibration of computations on these phthalocyanines, we have chosen first to investigate one of the simplest π–π interactions, i.e., two cofacial benzene rings, D, as embodied in the simple connected dimer, [2.2]paracyclophane (E). The latter molecule and related cyclophanes[7] are of considerable current interest, and lively discussion continues concerning various aspects of the electronic structure. Furthermore, a large body of PES data exists for cyclophanes. In the present contribution, we report a detailed DV-Xα analysis of the bonding in E with a view both toward addressing questions specific to this molecule and to approaching problems such as bandwidth/interplanar spacing relationships in low-dimensional conductors.



D



E

[2.2]Paracyclophane

The physical properties of [2.2]paracyclophane have been the subject of numerous studies since the reports of its synthesis[8] and crystal structure[9] 3 decades ago. A recent review by Heilbronner and Yang[10] reviews the electronic structure of these species, citing the early electronic structure work of Koutecky and Paldus[11] and its role in assignment of the PES spectra.

The importance in cyclophanes of mixing between bridge and π molecular orbitals of appropriate symmetry was first noted by Gleiter,[12] who explored the impact in E at the extended Hückel level. Since then, considerable discussion has centered around the relative contributions to splitting of cyclophane π levels arising from direct π overlap (generally attributed to "through-space effects"[13]) vs. that arising from differential mixing of π-orbitals with intervening bridge orbitals of appropriate symmetry ("through-bond effects"[13]). The study of the photoelectron spectra of the various cyclophanes, and their analysis using Koopmans' theorem and various molecular orbital methods, has been of real importance both in understanding the nature of the inter ring interactions in the cyclophanes themselves and in illuminating the general description of intramolecular "through-space" and "through-bond" couplings;[14–19] a thorough and convenient review is found in Heilbronner and Yang.[11]

Table I. Geometry[a] of [2.2]Paracyclophane Used in the DV-Xα Calculations[b]

bond	length, Å	ring deformation: plane 1	plane 2	dihedral angle, deg
C1–C2	1.39	C2,3,5,6	C2,6,1	12.6
C2–C3	1.39			
C1–C7	1.51	C2,3,5,6	C2,6,7	23.8
C7–C7′	1.57			
C6–H1	1.00			
C7–H2	1.05			
C3–C3′ (inter-ring dist)	3.09			

[a] Derived from ref 24 by assuming D_{2h} symmetry. [b] Refer to structure E for labeled structure.

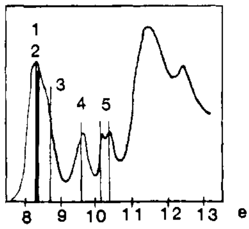


Figure 1. Photoelectron spectrum of [2.2]paracyclophane from ref 19, with vertical lines superimposed to indicate the ionization energies calculated in this work (see Table II).

The present paper is devoted to an analysis of the orbital ionization energies and the π–π interactions in [2.2]paracyclophane. We employ the first-principles discrete variational-method local-exchange (DV-Xα) technique, with self-consistent multipolar corrected potentials,[3] which has proven highly accurate in calculations on a number of small molecules, including benzene and *p*-xylene.[20] Ionization energies are calculated by using the transition-state method (vide infra).[22,23] The numerical results in this paper agree exactly with the most recent experimentally assigned level ordering[19] and match the ionization potentials extremely well. By combining these cyclophane results with a study of selected model systems, we can distinguish the ring-substitution and ring-distortion contributions to the energy splittings seen in the PE spectrum and can understand the remaining interactions in "through-space" and "through-bond" terms. Our calculations largely support Heilbronner's conclusion that the π overlap is predominant over, but influenced by, the mixing of the σ bridge bonds and that the effects of nonplanarity are very small; similar views have been expressed by Gleiter.[12,21] Our calculations permit quantitative estimates of each of the three major contributing factors to the orbital splittings in E.

Computational Method

The discrete variational Hartree–Fock–Slater, or DV-Xα, method is a first-principles local density technique originally developed by Baerends, Ros, and Ellis.[3a] This self-consistent-field solution of one-electron secular equations in the local exchange approximation yields the one-electron eigenvalues and orbital wave functions. The DV-Xα method has several advantages over other first-principles methods: due to its computational efficiency, much larger molecules can be handled than by Hartree–Fock calculations. Unlike scattered wave, or muffin-tin, Xα approaches,[22,23]

---

(7) (a) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65–70. (b) Vögtle, F.; Hohner, G. *Top. Curr. Chem.* **1978**, *74*, 1–29. (c) Vögtle, F.; Neumann, P. *Top. Curr. Chem.* **1974**, *48*, 67–129.

(8) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691–5704.

(9) Brown, C. J. *J. Chem. Soc.* **1953**, 3265–3270.

(10) Heilbronner, E.; Yang, Z.-Z. *Top. Curr. Chem.* **1983**, *115*, 1–55.

(11) Koutecky, J.; Paldus, J. *Collect. Czech. Chem. Commun.* **1962**, *27*, 599–617.

(12) Gleiter, R. *Tetrahedron Lett.* **1969**, *51*, 4453–4456.

(13) (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9. (b) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499–1509. (c) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696–701. (d) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245–251.

(14) Pignatoro, S.; Mancini, V.; Ridyard, J. N. A.; Lempka, J. H. *Chem. Commun.* **1971**, 142–143.

(15) Boekelheide, V.; Schmidt, W. *Chem. Phys. Lett.* **1972**, *17*, 410–413.

(16) Vogler, H. *Theor. Chim. Act (Berlin)* **1981**, *60*, 65–71.

(17) Boschi, R.; Schmidt, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 402–404.

(18) Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1974**, *57*, 151–159.

(19) Kovac, B.; Mohras, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314–4324.

(20) Doris, K.; Ratner, M. A.; Delley, B.; Ellis, D. E.; Marks, T. J. *J. Phys. Chem.*, in press.

(21) Gleiter, R.; Eckert-Makisic, M.; Schafer, W.; Truesdale, E. A. *Chem. Ber.* **1982**, *115*, 2009–2011 and references therein.

Table II. Comparison of Calculational Results for [2.2]Paracyclophane Ionization Potentials

peak[a] number		exptl[b]	DV-Xα[c]	CNDO/ S3[d]	Hückel/ empirical[b]	semiempirical[e]
1	b_{2g}	8.10 (5)	8.14	9.39	8.10	7.87
2	b_{3g}	8.10 (5)	8.17	9.39	8.10	8.24
3	b_{3u}	8.4 (1)	8.56	9.13	8.50	8.32
4	b_{2u}	9.65 (5)	9.55	9.88	9.90	9.46
5	b_{1u}	10.3 (1)	10.19	10.73		
	a_u		10.41	11.95		

[a] Peak numbers refer to Figure 2. [b] Reference 19. [c] This work. [d] Reference 27. [e] Reference 16.

the DV method approximates the wave functions rather than the potential (hence the word "variational"). The molecular potential can be augmented by including multipolar fitting functions, which reproduce covalent charge distributions very accurately.[3b,c] In addition, the numerical basis set used[3d] describes the "tail", or diffuse, regions of the wave functions more accurately than the small analytical basis set (Gaussian, Slater-type, etc.) used in most molecular orbital calculations. This is crucial in studies of π-orbital overlap beyond the carbon van der Waals radius, as in the cyclophane system; usual analytic basis functions are insufficient in the overlap region.

The success of the DV-Xα method with a multipolar density expansion in calculating the electronic structure of covalent molecules is well documented.[3b,c,20] The ionization energies are obtained by applying Slater's transition-state method,[22,23] which corrects for electron relaxation upon ionization; hence Koopmans' approximation, which is used in Hartree-Fock but is not valid in local density, is not invoked.[23] The basis set and density fitting functions used previously in benzene and *p*-xylene calculations[20] are sufficient to describe the valence electron density of [2.2]paracyclophane. Atomic basis orbitals are used, up to and including 3s,3p on carbon and only the 1s on hydrogen. The exact geometry of [2.2]paracyclophane was obtained from the single-crystal structure of Hope et al.,[24] and geometrical details are listed in Table I using the atom numbering scheme in E. The full D_{2h} symmetry of the molecule is employed.

Ionization Potential Results

Figure 1 shows the experimental gas-phase photoelectron spectrum of [2.2]paracyclophane.[19] Superimposed on this are transitions corresponding to the ionization energy results of our DV-Xα transition-state calculations. The numerical values are compared with the spectroscopic assignments in Table II. Both the assignments of the energy levels (Table III) and the corresponding peak positions are reproduced to within the experimental error. In addition, the ionization labeled 5 in the spectrum can be seen to consist of two peaks too closely spaced for unambiguous experimental resolution.[19] Our calculated values for the fifth and sixth ionization potentials average to the value experimentally assigned this region, and permit the higher and lower energy components of peak 5 to be assigned to b_{1u} and a_u, respectively.

Many approximate computational methods have been used to attempt assignment of the [2.2]paracyclophane photoelectron spectrum. Table II compares some of these results to those of DV-Xα. No previous calculation of any sort in the literature reproduce *both* the proper level ordering and the experimental peak positions. Heilbronner et al.[18,19,25,26] have used simple Hückel calculations and symmetry arguments, as well as comparison with synthetically substituted analogues, to arrive at their assignments. The CNDO study of Duke et al.[27],despite extensive manipulation of parameters, could not reproduce the spectroscopic level order. The success of the first-principles, nonparameterized DV-Xα method suggests that the resulting representations of the σ- and π-electron densities are accurate, and that further analysis of these distributions, to disentangle the nature of the physical interactions present, would be well justified.

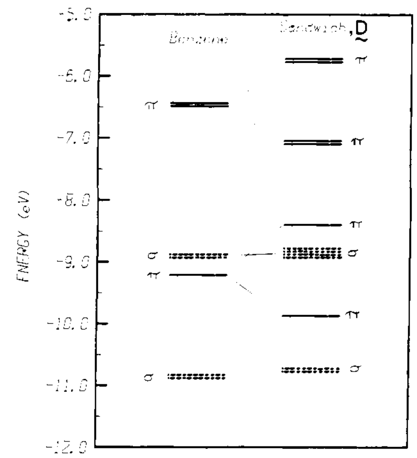


Figure 2. Comparison of the ground-state energies[28] of the highest occupied π-orbitals of benzene with those of a benzene "sandwich" dimer at 3.0-Å interplanar distance (the approximate distance between the planes of E). Solid lines indicate π levels, dashed σ.

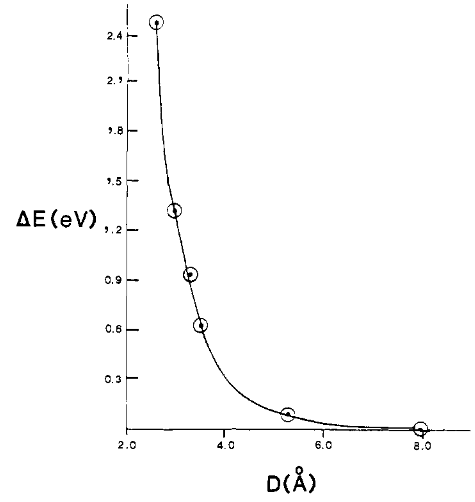


Figure 3. Change in the ground-state energy[28] splitting of benzene highest occupied π levels with changing interplanar distance of model D. This is the pure through-space splitting (depicted in Figure 2).

Through-Space vs. Through-Bond Effects in [2.2]Paracyclophane

To analyze the nature of π-π interactions, we will proceed in steps, analyzing, via fragments and models, the through-space interaction, the effects of ring distortion and bridge orbital mixing, and then the composite of these interactions in the complete molecule.

Through-Space Interaction. A benzene "sandwich" structure D is the simplest model applicable for examining only the through-space π-orbital splitting. The four (e_g) π-orbitals are split into two degenerate sets by the filled-orbital, closed-shell interaction (Figure 2). This splitting was calculated by using DV-Xα and is plotted as a function of the interplanar distance in Figure 3. In the region corresponding to real paracyclophane spacings, from about 2.6 to 3.4 Å, the splitting is roughly a linear function of separation. Kovac et al.[19] have also found, by comparison of a number of different cyclophanes, that the experimental splitting is roughly linear in this distance region. However, the splitting

---

(22) Slater, J. C. "Quantum Theory of Molecules and Solids"; McGraw-Hill: New York,. 1974; Vol. 4.

(23) (a) Johnson, K. H.; Smith, F. C., Jr. *Phys. Rev. B* **1972**, *5*, 831-843. (b) Johnson, *Ann. Rev. Phys. Chem.* **1975**, *251*, 39-57.

(24) Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr., Sect B* **1972**, *B28*, 1733-1743.

(25) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936-967.

(26) Kovac, B.; Allen, M.; Heilbronner, E. *Helv. Chim. Acta* **1981**, *64*, 430-448.

(27) Duke, C. B.; Lipari, N. .; Salaneck, W. R.; Schein, L. B. *J. Chem. Phys.* **1975**, *63*, 1758-1767.

Table III. Major Contributions to the Orbital Populations of E[a]

		ring C(2)		end C(1)				
orbital	energy, eV	π	σ	π	σ	bridge C(7)	bridge H(2)	ring H(1)
b_{2g}(unoccd)	−1.80	0.51	-	0.31	0.06	0.13	-	-
b_{2g}(HOMO)	−5.66	0.27	-	0.58	0.11	0.02	0.01	-
b_{3g}	−5.78	0.98	0.02	-	-	-	-	-
b_{3u}	−6.18	0.31	-	0.40	0.11	0.17	0.01	-
b_{2u}	−7.06	0.98	-	-	0.01	-	-	-
b_{1u}	−7.85	0.51	0.09	0.07	0.18	0.13	0.02	-
a_u	−8.20	-	0.31	-	0.29	0.05	0.14	0.21
b_{1g}	−8.48	-	0.31	-	0.35	-	0.02	0.29
b_{3g}	−8.94	-	0.14	-	0.05	0.28	0.52	-
$a_g(\pi)$	−8.94	0.60	0.04	0.05	0.03	0.23	0.05	-
$b_{1u}(\pi)$	−9.21	0.21	0.20	0.23	0.10	0.23	0.02	0.01
a_g	−9.36	-	0.30	0.01	0.17	0.47	0.02	0.03
a_u	−9.55	-	0.07	-	0.03	0.34	0.45	0.11
b_{2g}	−9.65	-	0.06	0.07	0.33	0.43	0.07	0.02
b_{3u}	−10.33	-	0.03	-	0.26	0.67	0.01	0.01
b_{2u}	−10.37	-	0.49	-	0.23	0.11	0.13	0.04
b_{3g}	−10.63	-	0.58	-	0.19	0.02	0.13	0.04
b_{2u}	−11.11	-	0.48	-	-	0.18	0.03	0.16
b_{3u}	−11.27	-	0.20	0.09	0.17	0.32	0.16	0.17
$a_g(\pi)$	−11.58	0.13	0.11	0.24	0.01	0.43	0.05	0.19
b_{1g}	−11.75	-	0.03	-	-	0.53	0.08	-

[a] Dash indicates <1%.

Table IV. Major Contributions to the Populations of Orbitals upon Bending *p*-Xylene. Numbering as in E

level	ring π(C2,3, 5,6)	end π(C1,4)	end σ(C1,4)	methyl C7,8	methyl H(2)
b_1(HOMO)					
planar	0.29	0.60	0.00	0.02	0.08
bent	0.28	0.51	0.10	0.01	0.05
b_2					
planar	1.00				
bent	0.99				

they considered was by necessity an approximation to the pure π splitting, since they did not know the extent of a σ mixing into the lower experimental ionization energies, and instead compared the benzene HOMO ionization energy to the lowest ionization energies of the cyclophane series. Our computation supports their argument. (In tight-binding band theory this through-space splitting would approximate one-half the bandwidth of an infinite stack of planar benzenes, the simplest model of an aromatic-molecule electronic conductor.)

Effect of Ring Alkyl Substitution, Distortion from Planarity, and Bridge Orbital Mixing. Three effects that invalidate the σ/π separation of the benzene sandwich model in the actual molecule E are alkyl substitution of the benzene monomers, distortion of the aromatic π systems from planarity, and the mixing of bridging σ-orbitals upon "dimerization" of bent *p*-xylenes, forming E. The first step in quantifying these effects is to ascertain how the electronic structure of benzene is altered upon alkyl substitution of the 1,4-positions. For this we employ *p*-xylene as a model. The DV-Xα method accurately reproduced the photoelectron peak (ionization) energies and assignments for this molecule.[20] A comparison of the ground-state orbital energies[28] in Figure 4 shows that the degeneracy of the highest occupied π-orbitals of benzene is removed upon substitution with two methyls. The upper *p*-xylene π levels are split by 0.6 eV, a nontrivial effect. The upper π level, b_1 in Table IV, consists mostly (60%) of π density on the methyl-substituted ring carbons (corresponding to C1 and C4 in E); the second π level, b_2, has no density there, but on the unsubstituted ring carbon atoms instead.

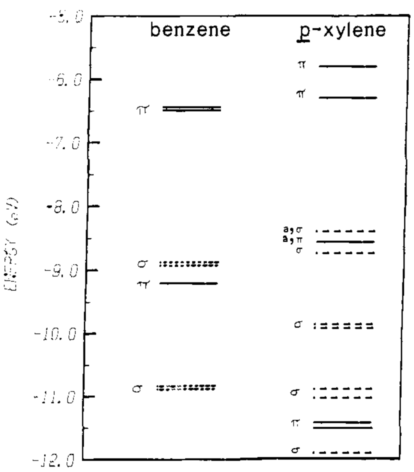


Figure 4. Comparison of the ground-state energies[28] of the occupied benzene orbitals with those of *p*-xylene. This demonstrates the effects of dimethylation of benzene in the para positions.

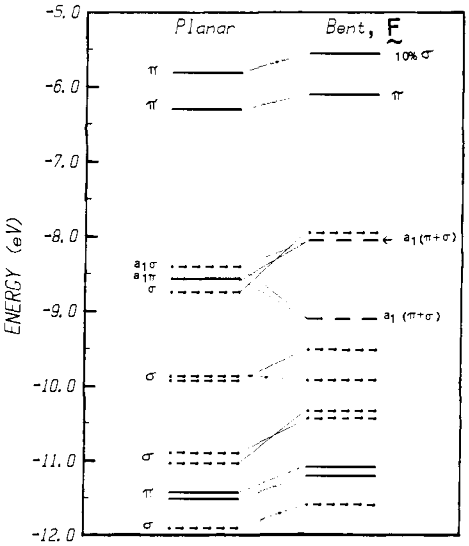


Figure 5. Comparison of the ground-state energies[28] of the highest occupied orbitals of planar *p*-xylene with those of *p*-xylene bent into half a paracyclophane, or model F. Note that the energy separation of the two highest levels does not change. Change in σ/π composition is indicated by mixing of solid (π) with dashed (σ) lines; see Table IV for the orbital populations.

---

[28] For orbitals of the same diffuseness and energy range, the qualitative energy level diagram does not change when a transition-state calculation is used to find the exact ionization energies. Therefore this procedure is not necessary when only comparing a series of like models and not seeking to match experimental spectra. The ground-state one-electron orbital energies are therefore used.

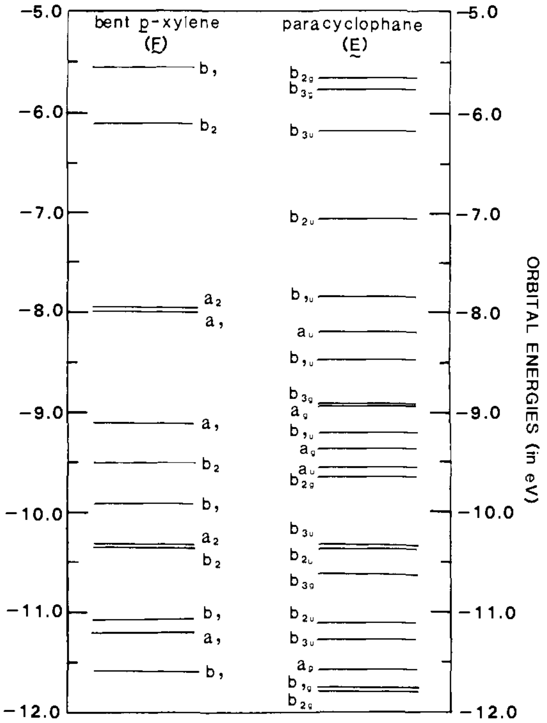
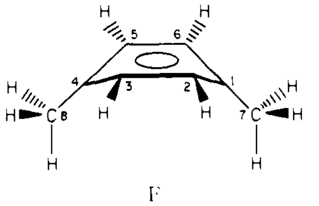


Figure 6. Comparison of the ground-state orbital energies[28] of F with those of E (an actual paracyclophane). This represents "dimerization" of the subunits of E; the resulting splittings are due to a combination of through-space (Figure 3) and through-bridge-bond interactions, which are separated in this work (see text).

Ring bending, forming model F (with the dimensions of half a paracyclophane), raises the energy of each π-orbital equally,



F

preserving the 0.6-eV splitting caused by methyl substitution (Figure 5). This result confirms earlier, more qualitative molecular orbital studies[11,19,29] and observations from trends in PES data:[29] π-level splittings in substituted benzenes are caused primarily by substituent effects, not by ring distortions when present. Indeed, the more general conclusion has been reached[10,30] that small amounts of bending and twisting have very small effects on the ionization energies. This has important consequences in model calculations of the bandwidths of organic metals, since it implies that planarity may often be assumed without significantly changing the relative positions of π levels in the aromatic subunits.

Distortion of *p*-xylene to the geometry of model F does affect the orbital populations, however. Table IV shows the introduction of 10% σ character into the upper π level, b_1, upon bending. This σ admixture can be seen in all subsequent models in this work and in the actual paracyclophane π composition (Table III, b_{2g} and b_{3u} levels). Distinction between this σ contribution to the π levels of E and any due to through-bond effects is simple to establish: any carbon atom σ contributions in the π molecular orbitals of E, but not in those of the monomer F, must be due to bridging orbital effects on the π system in the cyclophane. In particular, no methyl carbon atom character mixes into the π levels of F; appearance of such admixture in E would indicate through-bond π-orbital interactions.

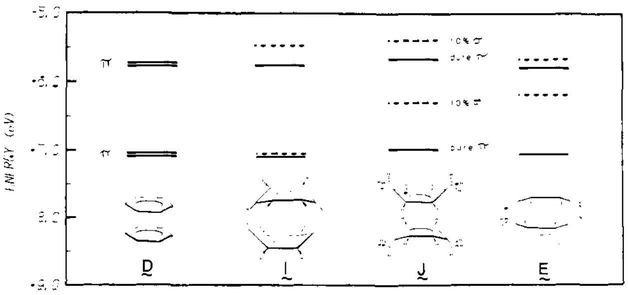
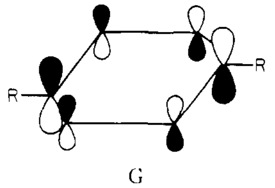


Figure 7. Ground-state energies[28] of the highest occupied (π) orbitals of (a) benzene sandwich D at 3-Å separation (b) face-to-face bent benzenes, model I, (c) back-to-back bent *p*-xylenes, model J, and (d) actual [2.2]paracyclophane E from Figures 1 and 7 and Tables II and III. Comparison of Figure 7 part a with b demonstrates the increase in through-space splitting of the G set of π-orbitals (dashed) upon bending the ends toward one another, as in E. Dashed lines indicate the 10% σ admixture into this set created by bending (see Tables III and IV). An analogous decrease in the splitting of this set is seen in J due to the increased distance between the ends. Further discussion is in text.

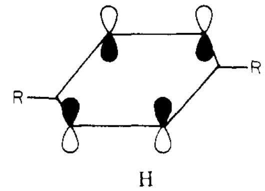
Interaction of Paracyclophane Subunits. The above results indicate that while ring deformation has a major effect on π-orbital compositions and ionization energies, it does not significantly affect the energy separations of the occupied π levels in the individual monomer subunits. Similarly, another calculation indicated that bending the subunits of D (to the geometry of the individual rings in E) so that they remain "parallel" (i.e., all intermolecular distances are equal, at 3.0 Å) results in no significant change (<0.1 eV) in the through-space splittings; the π levels are slightly nondegenerate due to the bending (symmetry lowering) in the monomer, but both splittings of the π levels are 1.3 eV, the through-space value in D at 3.0 Å. This demonstrates that if only the bandwidth, or through-space splitting, is of interest in a uniformly buckled stack (e.g., the Sn phthalocyanine polymer[6c]), the calculation can, to a good approximation, be carried out on planar subunits. However, absolute energy values such as ionization potentials will be changed by this assumption.

A comparison of the orbital energies[20,28] of subunit F with those of actual paracyclophane, E, will give an indication of what splittings occur upon "dimerization" (Figure 6). Through a series of models we shall now attempt to distinguish what portion of the splittings seen in Figure 6 is due to through-space orbital interactions, as in Figure 2, and what portion is due to through-bridge-bond interactions.

If two distorted benzenes are face to face at the paracyclophane distance, 3 Å, there will be a slight difference in the through-space splittings of the two pairs of π molecular orbitals. This occurs because one of the pairs derives from the *p*-xylene b_1 set (G), which is centered predominantly on the alkyl-substituted carbon atoms; these orbitals are brought closer together spatially by the inward ring distortion in E. The other (b_2) set of overlapping benzene π levels, the H set, is unaffected by distortion because it has nodes at the end (alkyl-substituted) carbon atoms.[31] Thus the H set, corresponding to the b_{3g} and b_{2u} levels of paracyclophane (Table III), retains the pure "through-space" splitting seen in the benzene sandwich model D, independent of any ring distortion. The DV-Xα results for the bent benzene sandwich model permit quantitative estimation of the difference in π-π interaction energies brought about by bending. Figure 7 compares the four highest



G



H

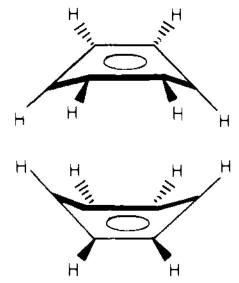
---

(29) Gleiter, R.; Hopf, H.; Eckert-Maksic, M.; Noble, K.-L. *Chem. Ber.* **1980**, *113*, 3401-3403.

(30) Honegger, E.; Heilbronner, E.; Wiberg, K. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *31*, 369-381.

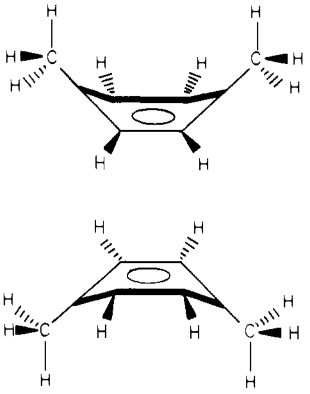
(31) Yang, Z.-Z.; Kovac, B.; Heilbronner, E.; Eltamany, S.; Hopf, H. *Helv. Chim. Acta* **1981**, *64*, 1991-2001.

occupied levels of D (extreme left) to those of I, which is a paracyclophane with the bridging CH_2CH_2 groups replaced by normal aromatic C–H bonds.[32] The through-space splitting is still 1.32 eV, but the G set, shown dashed in Figure 7, exhibits 0.3 eV greater interaction in I than D.



I

Having established that bending does affect the basic benzene orbital energy splittings in the "face-to-face", centrosymmetric dimer I, we now consider the effect of methyl substitution of the dimer *without* bonding of the subunits to create the cyclophane. Actual bent *p*-xylene subunits cannot be placed at the interring distance of E without strong nonbonded repulsion of methyl hydrogen atoms. We therefore consider another model of subunit interactions at 3-Å separation with no bridge bonding (or "through-bond" interactions). This alternative model, J, consists of "back-to-back" bent *p*-xylenes F at 3-Å interplanar separation. This model allows us to examine the through-space interaction of the pure π levels (H) of two isolated bent *p*-xylenes. Figure 7 reveals that, as expected, the H set or pure π levels of J (solid lines) do not deviate significantly from the "through-space" splitting of D, ca. 1.32 eV (the other set of levels, G, which contain roughly 10% σ character, is split by less, which is expected given the greater spatial separation of the methyl-substituted carbon atoms). In addition, the origins of two π sets of J are found to be ca. 5.8 and 6.4 eV, which are split by exactly the 0.6 eV found in the monomer F (Figure 6). These origins in J are, however, almost 0.3 eV lower than those of F, suggesting polarization stabilization upon dimerization.



J

The π-orbital populations of the inverted dimer model J remain exactly the same as those listed in Table IV for bent *p*-xylene (F). Both levels with origins in the upper, b_1, orbital retain the 10% end σ character caused by ring distortion. The pure π level, b_2, splits to form two pure π levels (solid lines in Figure 7). This observation is essential in separating the true through-bond effect from all other structural factors, since even in J no methyl carbon character is present in the upper π levels. Any methyl character seen in the corresponding levels of E (in Table III) must be due to bridge-bonding and not lowering of the symmetry.

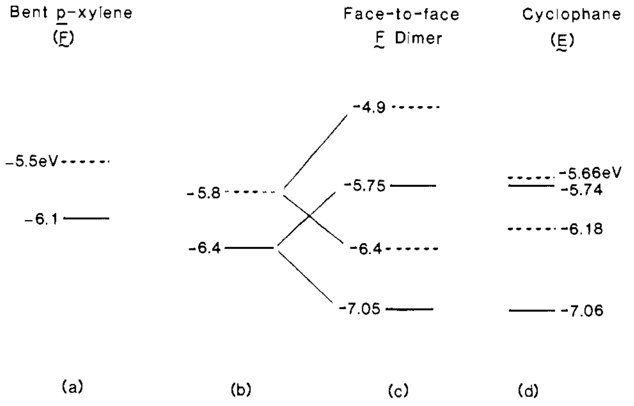


Figure 8. Ground-state energies[28] of the highest occupied (π) levels of (a) model F, as in Figure 6, (b) the same, adjusted to the energies of the original, or unsplit, orbitals of model J, Figure 7c, (c) an imaginary dimer formed from the subunits in b, with the through-space splittings of model I (Figure 7b), and (d) actual paracyclophane, from Figures 1 and 7 and Table I and III. The differences between parts c and d of Figure 8 are due only to bridge-bonding or through-bond effects. See text.

The through-bond interaction energy cannot be obtained by comparing the π HOMOs of I with E because of the strong influence of alkyl substitution on orbital energies (Figure 4). Similarly, comparison of J with E would underestimate the decreasing of the splitting of the σ-mixed π set G due to through-space interaction, since J underestimates that splitting.

Numerical values of through-bond effects can, however, be extracted from the combined results on models D, F, I, and J. Figure 8 illustrates the thought processes and assumptions involved in forming E from F. The π levels of the monomer, F (Figure 8a), are lowered by the 0.3-eV stabilization energy found above in model dimer J, resulting in Figure 8b. We know that the pure π levels (solid lines) are split by the through-space value of 1.32 eV at 3-Å ring separation. Therefore this splitting is depicted in Figure 8c centered above the pure π orbital H in Figure 8b. However, upon ring bending, the splitting of the σ mixed set G will be greater than this value by (at least) the 0.3 eV found in I (Figure 7) and will be asymmetric about the origin, ca. 0.66 eV down and 0.96 eV up, as in I. This latter step assumes that this splitting does not change appreciably upon methyl substitution; this is a reasonable assumption, since no methyl carbon character appears in the populations of the π levels of F (Table IV). Therefore the G set of a bent *p*-xylene dimer would be split similarly to that of the face-to-face bent benzene dimer I (1.6 eV).

Figure 8c should represent the face-to-face bent *p*-xylene dimer without through-bond effects but including alkyl substitution, ring distortion, and through-space effects. Therefore the differences between the π-level configuration in Figure 8c and that of the actual cyclophane molecule, E, in Figure 8d, are solely due to bonding of the subunits.

The actual through-bond interaction energies in E can thus be reasonably well partitioned from all other effects. The total decrease in the through-space splitting of the G set of π-orbitals due to mixing with bridging orbitals is ca. 1.0 eV (from 1.5- to 0.5 eV separation in energy, as can be seen in Figure 8). This decrease is a combination of two σ/π interactions: the HOMO (b_{2g}) is lowered by ca. 0.8 eV, and the third occupied π level (b_{3u}) is raised by ca. 0.2 eV. The latter interaction was identified by other investigators[12,19,21] and consists of an occupied bridging orbital of low energy (perhaps ca. −10 eV in Figure 6) mixing with the difference of two G ring orbitals, as pictured in Figure 9a. This mixing produces a higher, mostly π level, the b_{3u} in Figure 8d, and a lowered, mostly bridge σ level, b_{3u}, which can be found in Table III and Figure 6 at −10.3 eV. Both are occupied, since the original ring and bridge components were also. The high b_{3u} orbital has 12% bridge carbon contribution as a result of this mixing (Table III).

The interaction which lowers the b_{2g} (highest occupied) orbital in Figure 8 has not been previously identified. Since the orbital

---

(32) An analogous scheme for distinguishing through-bond and through-space interactions has been used in substituted cyclobutanes ((a) Pasto, D. I.; Chipman, D. M.; Worman, J. J. *J. Phys. Chem.* **1982**, *86*, 3981–3989) and by Kabayashi et al. in triptycene ((b) Kabayashi, T.; Kubota, T.; Ezumi, K. *J. Am. Chem. Soc.* **1983**, *105*, 2172–2174).

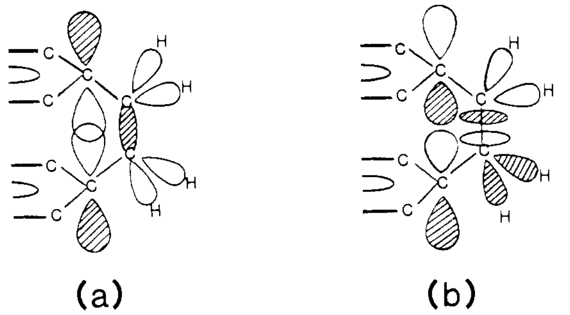


Figure 9. Depiction following ref 19 of the interactions responsible for the through-bond decrease in the through-space splitting of the G set of π-orbitals of E (demonstrated in Figure 8, c → d). (a) The occupied bridge σ-orbital and difference combination of ring G π-orbitals, all of which create a raised b_{3u} orbital in Figure 8d. (b) The unoccupied bridge σ-orbital and the sum combination of G ring π-orbitals, which create a lowered b_{2g} (HOMO) in Figure 8d.

energy is lowered, this must result from the mixing of the occupied ring b_{2g} orbital with an unoccupied bridge b_{2g} orbital of higher energy. This would create a lowered occupied orbital, the HOMO, and a corresponding high-energy virtual orbital of b_{2g} symmetry. Table III lists this orbital and gives the combination of ring π- and bridge σ-orbitals, which are shown in Figure 9b. The HOMO exhibits only 2% bridge contribution to the atomic populations, and the corresponding empty b_{2g} is only 13% localized on the bridge.

Conclusions

Our results provide quantitative estimates of the importance of through-space interactions in the cyclophanes. One set of π-orbitals remains essentially unaltered by σ character upon alkyl substitution, ring deformation, and bridge-bonding, despite the presence of σ basis orbitals of proper symmetry to mix with these molecular orbitals. The through-bond and ring-deformation effects are clearly separable using the basis orbital populations and the molecular orbital energies of carefully selected models. Bending, while mixing some σ character into one of the π-orbitals of *p*-xylene, appreciably changes neither the splitting of these two highest occupied π levels induced by methyl substitution of benzene nor the through-space splitting. This observation is relevant to studies of the bandwidths of partially occupied "organic metal" bands in systems such as TTF-TCNQ[1] or the stacked phthalocyanine conductors.[6,33] Planarity may be assumed for the aromatic subunits of these stacks without substantially changing this "bandwidth", which is based on the upper π-level splittings. The only exceptions will occur for very large distortions from planarity, where the bandwidth is substantially reduced; a case in point is the highly buckled octamethyltetrabenzoporphyrin system, which forms a linear-chain conductor whose bandwidth is apparently so small that its description lies at the atomic limit of the Hubbard model.[34]

In addition, Figure 3 is a reminder of the rapid falloff of through-space splittings of highest occupied π levels with increasing distance. This splitting corresponds to half the tight-binding bandwidth of stacked organic conductors,[1] and so our results are important for synthetic design of such systems. Much greater intrastack distances than the paracyclophane distance (ca. 3 Å) lead to very narrow bandwidths and, hence, localization of charge carriers.

Through-bond effects could be seen in the models as stabilization of the upper π level of E and destabilization of the third occupied π level (Figure 8). The presence of actual direct mixing of bridging orbital character into both of these π levels can be clearly seen from model studies and the orbital populations of E. Interaction with a deep, occupied bridge orbital raises the energy of the b_{3u} (third π level) by 0.2 eV and mixes 17% bridging carbon character into its wave function (Table III). Similarly, interaction of a low-lying unoccupied bridge orbital with the b_{2g} π HOMO lowers the energy of the latter by 0.8 eV. This latter through-bond stabilization has not been remarked on previously.[12,18,20] The present study has thus quantified the total through-bond effect in [2.2]paracyclophane at ca. 1.0 eV, as compared to the larger 1.3-eV through-space splitting so well established in the literature.

We have shown that the DV-Xα method is a reliable, first-principles method for obtaining quantitative results, such as ionization potentials, in good agreement with experiment. In addition, the method allows separation of functional group interactions relevant for spectroscopy, through study of the molecular orbitals of model compounds as well as parent molecules. This approach should be useful in studies of many types of orbital interactions, including electronic transport in organic conductors.

Acknowledgment. This research was generously supported by the Office of Naval research (to T.J.M.), by the Chemistry Division of the NSF (to M.A.R.), and by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR79-23573). We are grateful to B. Delley and F. Kutzler for their contributions to program development and to W. Pietro for helpful dicussions.

Registry No. [2.2]Paracyclophane, 1633-22-3.

---

(33) (a) Schramm, C. S.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702–6713. (b) Marks, T. J.; Kalina, D. W. In ref 1a, Vol. 1, pp 197–331. (c) Stojakovic, D. R. Ph.D. Thesis, Northwestern University, Evanston, IL, 1978.

(34) Hoffman, B. M.; Phillips, T. E.; Soos, Z. G. *Solid State Commun.* **1980**, *33*, 51.