10542 J. Am. Chem. Soc. 1992, 114, 10542-10547

Theoretical Study of [4]Paracyclophane and Its Dewar Benzene and Prismane Valence Isomers

Stefan Grimme

Contribution from the Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, W-5300 Bonn 1, Germany. Received June 1, 1992

Abstract: Ab initio calculations were carried out for [4]paracyclophane (**1**) and its Dewar benzene (**2**) and prismane (**3**) valence isomers. The compounds were studied using AO basis sets ranging from 6-31G type to such of triple-ζ type including d and f functions on the carbon atoms and p functions at the hydrogen atoms. Complete geometry optimizations were performed with basis sets up to double-ζ quality. The critical geometrical distortion angle of the benzene ring of **1** is calculated to be 29.7° which is 5° larger than for the [5]paracyclophane molecule. The calculated strain energies of the three isomers (91.3, 1.6, and 4 kcal/mol for compounds **1**–**3**) show that only the relative energy of the benzene isomer is affected by the short $(CH_2)_4$ chain. Furthermore it is found that the SCF approximation is not suitable for the calculation of the energy difference between the benzene and the corresponding Dewar benzene form due to a partial diradicaloid character of **1**. The employment of MP2, MP4SDTQ, CAS-SCF, and MRD-CI correlation energy treatments yields an estimated energy difference of $\Delta E = 0 \pm 3$ kcal/mol between **1** and **2**. Corrected ΔE values obtained from various semiempirical treatments agree with this prediction. Additionally the lowest triplet and three of the lowest excited singlet states of **1** were considered using the MRD-CI method. The calculated excited-state energies are in reasonable agreement with the experimental UV spectrum of **1**. On the basis of the calculational results the [4]paracyclophane molecule is classified as benzene-like due to the topological similarity to the parent compound.

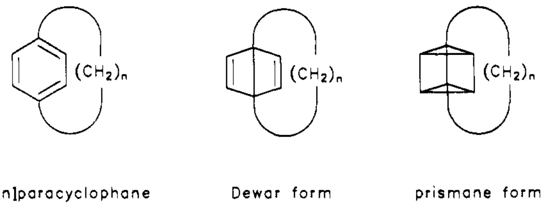
I. Introduction

The family of the [*n*]paracyclophanes (see Chart I) has attracted considerable interest in recent years.[1,2] Theoretical and experimental studies of the compounds with $n > 4$ have shown that reducing the length of the $(CH_2)_n$ chain forces the benzene ring into a nonplanar, boat-type geometry. These observations have stimulated a very controversial but fruitful discussion on the concept of aromaticity.[2-5]

Experience with the $n = 6$ and $n = 5$ paracyclophanes has demonstrated that the reduced chain length also results in a significant decrease of the thermal stability of the compounds. Since [5]paracyclophane could not be isolated in a pure form at room temperature,[4] it is suggested that the [4]paracyclophane molecule would be very unstable if it were generated. Another property which is strongly related to the bending of the benzene ring with decreasing *n* is the electronic absorption spectrum of the aromatic forms. An increasing red shift of the first three benzene-type transitions (${}^1A_{1g} \rightarrow {}^1B_{1u}, {}^1B_{2u}, {}^1E_{1u}$) has been observed experimentally[6] and has also been studied theoretically for the compounds with $n > 4$.[7] An analogous dependence was found in the phosphorescence spectra of substituted [*n*]paracylophanes ($n = 10, 8, 7$) for the $T_1 \rightarrow S_0$ transitions.[8]

Experimental evidence for the existence of the smallest member in the [*n*]paracyclophane series ($n = 4$) was first reported by Bickelhaupt and co-workers in 1987.[9] Irradiation of the Dewar benzene form (**2**) in trifluoroacetic acid at −20 °C results in an interception of **1** by nucleophilic attack of the solvent at the bridgehead positions. Similarly to the photoreactions of the $n = 5$ and $n = 6$ Dewar benzene compounds[10-12] the formation of the $n = 4$ prismane isomer (**3**) was observed as a side product. The photochemical route was also used in 1988 by Tsuji and Nishida[13] to produce **1** in high yield at 77 K. Besides alcoholic interception products these authors have also reported UV spectra of **1** and two ring substituted compounds ($R = CH_2OMe, CO_2Me$) which support the existence of [4]paracyclophane as an unstable molecule (rapid decomposition above −100 °C). In their article it was also noted that the photochemical interconversion between the benzene and the Dewar benzene form is completely reversible, which has also been observed for the $n = 6$ compounds.[11,12,14]

Chart I



(1) (2) (3)

The relative energetics of the benzene and Dewar benzene forms as a function of *n* is of particular interest. Semiempirical and ab initio theoretical methods differ substantially in the prediction of the chain length *n* for which the Dewar isomer becomes more stable than the benzene form. While the former methods indicate a breakpoint at $n = 5$–6[15-17] the extrapolation of ab initio SCF results suggest a value of $n = 4$.[18] The experimental measurements of the reaction enthalpy in the case of ring substituted $n = 6$ compounds (≈5 kcal/mol[11,12]) could not rule out any prediction since it has been shown that substituents have a significant influence on the isomerization energy.[18] Furthermore, in several

---

(1) (a) *Cyclophanes*; Keetin, P. M., Rosenfeld, S. M., Eds.; Academic Press: 1983. (b) Vögtle, F. *Cyclophan-Chemie*. B. G. Teubner Verlag Stuttgart: 1990.

(2) Bickelhaupt, F. *Pure Appl. Chem* **1990**, *62*, 373.

(3) Cram, D. J. Cram; J. M. *Acc. Chem. Res.* **1971**, *4*, 204.

(4) Jenneskens, L. W.; Kanter, de F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; Wolf, de W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1985**, *107*, 3716.

(5) Rice, J. E.; Lee, T. J.; Remington, R. B.; Allen, W. D.; Clabo, D. A.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 2902.

(6) Allinger, N. L.; Walter, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 9267.

(7) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100.

(8) Hopf, H.; Haase, M.; Hunger, J.; Tochtermann, W.; Zander, M. *Chem. Phys. Lett.* **1986**, *127*, 145.

(9) Kostermans, G. B. M.; Bobeldijk, M.; Wolf, de W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471.

(10) Kapahnke, P. Ph.D. *Thesis*. Universität Braunschweig, 1988.

(11) Dreeskamp, H.; Kapahnke, P.; Tochtermann, W. *Radiat. Phys. Chem.* **1988**, *32*, 537.

(12) Bokisch, F.; Dreeskamp, H.; Haugwitz, von T.; Tochtermann, W. *Chem. Ber.* **1991**, *124*, 1831.

(13) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1988**, *110*, 2157.

(14) Kammula, S. L.; Iroff, L. D.; Jones, M.; Straten, Van J. W.; Wolf, De W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1977**, *99*, 5815.

(15) (a) Bokisch, F. Diploma Thesis, Universität Braunschweig, 1990. (b) Bokisch, F.; Rayez, J.-C.; Dreeskamp, H.; Liotard, D.; Duguay, B. *Theor. Chim. Acta*, in press.

(16) Jenneskens, L. W. Ph.D. Thesis, Vrije Universiteit, Amsterdam, 1986.

(17) Bickelhaupt, F.; Wolf, de W. H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 459.

(18) Peyerimhoff, S. D.; Arnim, von M. *Theor. Chim. Acta.*, in press.

0002-7863/92/1514-10542$03.00/0 © 1992 American Chemical Society

Table I. Summary of Employed AO Basis Sets

notation		description[a]	ref
6-31G	C	(10s,4p) → [3s,2p]	*b*
	H	(4s) → [2s]	*b*
DZ+d	C	(8s,4p) → [4s,2p] +d (0.8)	*c*
	H	(4s) → [2s]	*d*
DZP		as DZ+d	*c*
	H	+p (0.8)	
TZP	C	(9s,5p) → [5s,3p] +d (0.8)	*e*
	H	(5s) → [3s] +p (0.8)	*f*
TZ2P	C	(9s,5p) → [5s,3p] +2d (0.46,1.39)	*e*
	H	(5s) → [3s] +2p (0.46,1.39)	*f*
TZP+f		as TZP	*e*
	C	+f (0.6)	

[a] The notation $(i,j) \rightarrow [k,l]$ refers to i primitive s and j primitive Gaussian p functions contracted to k Gaussian s groups and l Gaussian p groups. [b] Ref 43. [c] Exponents and contraction coefficients from ref 44 (8s,5p). The outermost p-function was discarded and the (8s,4p) set uncontracted to [5111/31]. [d] Exponents and contraction coefficients from ref 45. The s-functions were uncontracted to [31]. [e] Exponents from ref 45, contraction coefficients from ref 46. [f] Exponents and contraction coefficients from ref 45. The s-functions were uncontracted to [311].

studies it has been suggested that the reduced chain length *n* affects predominantly the energetics of the benzene form which means that the potential minima of the [*n*]paracyclophane molecules are "moved" on a reaction pathway toward the barrier for the thermally "forbidden" disrotatory electrocyclic reaction.[10,11,18] Within this model it is expected that for large negative values of the isomerization energy **1** → **2** (the Dewar form is more stable) the reaction becomes thermodynamically "allowed".

In this work high quality ab initio calculations on the structures and energetics of [4]paracyclophane and two of its valence isomers are presented. Up to now only one ab initio work has been reported for [4]paracyclophane using the STO-3G basis set,[19] while numerous (semi)empirical[7,15,16,20] and ab initio studies[5,18,21-23] have been performed for the $n = 7$–5 compounds. Special attention has been placed on methodological consistency and on the relevance of the calculations with respect to experimental work. Therefore ab initio methods with different levels of sophistication are employed to obtain chemically meaningful results, particularly for the isomerization energies. Additionally the results of excited-state calculations are included to assign and interpret the electronic ultraviolet spectrum of **1** reported by Tsuji and Nishida.[13]

II. Theoretical Details

Self-consistent field (SCF) theory using various Gaussian basis sets (see Table I) ranging from 6-31G to triple-ζ plus polarization function quality were used to obtain initial values for the energy differences between the three valence isomers. The ab initio SCF and second-order Møller–Plesset perturbation theory (MP2)[24] calculations and the geometry optimizations were carried out with the TURBOMOLE program package.[25] For the MP4 calculations the Gaussian 90 program system[26] was used. The CAS-SCF (complete active space) calculations were performed with the SIRIUS program of Jensen and Ågren.[27] Complete geometry optimization of all geometrical parameters within the constraint of C_2 symmetry was performed with basis sets up to DZP quality. All energy minima were obtained with a precision of 10^{-6} au. Thus the calculated bond lengths (bond angles) were obtained with a precision of 5×10^{-4} Å (0.1°).

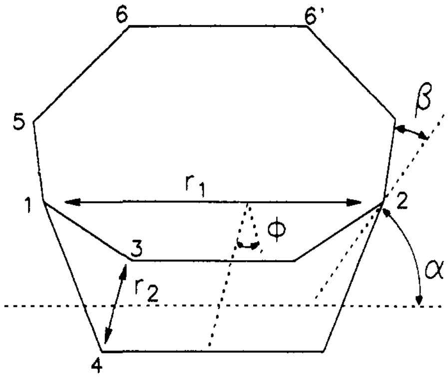


Figure 1. Definition of the most important deformation angles α, β, and ϕ and the bond distances r_1 and r_2.

Table II. Comparison of Calculated Geometric Parameters (SCF-DZP Optimized Structures) Characteristic for the Inherent Strain of $n = 6$–4 [*n*]Paracyclophanes and Their Dewar Benzene and Prismane Valence Isomers[d]

	α (deg)	β (deg)	ϕ (deg)	r_1 (Å)	r_2 (Å)
	Benzene Isomer				
$n = 4$ (C_2)[a]	29.7	38.2	145.9	2.657	2.374
$n = 5$ (C_S)[b]	23.5	28.7	152.8	2.710	2.385
$n = 6$ (C_2)[b]	18.8	20.6	158.0	2.750	2.381
$n = \infty$ (benzene)	0.0	0.0	180.0	2.773	2.401
	Dewar Benzene Isomer				
$n = 4$ (C_2)	81.4	21.5	116.1	1.567	2.583
$n = 5$ (C_S)[b]	81.3	30.9	114.8	1.580	2.586
$n = 6$ (C_2)[b]	80.7	27.7	114.8	1.600	2.584
$n = \infty$ (dewar bz)[c]	81.7	24.5	117.4	1.554	2.596
	Prismane Isomer				
$n = 4$ (C_2)	90.2	33.8	60.4	1.540	1.513
$n = \infty$ (prismane)[c]	90.0	42.5	60.0	1.548	1.506

[a] Values of $\alpha = 28.3$ and $\beta = 39.5°$ have been reported by Jenneskens et al.[19] using the STO-3G basis set. [b] 6-31G basis set, from ref 18. [c] Similar calculated geometric data have been reported by Disch and Schulman.[47] [d] For comparison the data of the parent compounds benzene, Dewar benzene, and prismane are also given.

The semiempirical calculations were performed with the MOPAC 6.0 program system[28] which was modified to allow comparative MP2 and SDCI calculations with the semiempirical MNDOC-Hamiltonian.[29]

Multireference CI calculations (MRD-CI) were undertaken in the standard manner of Buenker and Peyerimhoff[30] using Hartree–Fock MOs of the ground-state wave function as the molecular basis. Estimation of the full CI energy is done in analogy to the Davidson correction.[31]

III. Results and Discussion

A. Geometry. The geometry optimization of [4]paracyclophane (**1**) and its valence isomers **2** (Dewar benzene form) and **3** (prismane form) was undertaken at the SCF level employing 6-31G, DZ+d, and DZP basis sets. The differences between the optimized geometries are generally small (bond length < 0.01 Å, bond angles < 1°), especially for the most important deformation angles α and β (see Figure 1) which are found to agree within

---

(19) Jenneskens, L. W.; Louwen, J. N.; Wolf, de W. H.; Bickelhaupt, F. *J. Phys. Org. Chem.* **1990**, *3*, 295.

(20) Schmidt, H.; Schweig, A.; Thiel, W.; Jones, M. *Chem. Ber.* **1978**, *111*, 1958.

(21) Remington, R. B.; Lee, T. J.; Schaefer III, H. F. *Chem. Phys. Lett.* **1986**, *124*, 199.

(22) Lee, T. J.; Rice, J. E.; Remington, R. B.; Schaefer III, H. F. *Chem. Phys. Lett.* **1988**, *150*, 63.

(23) Lee, T. J.; Rice, J. E.; Allen, D. A.; Remington, R. B.; Schaefer III, H. F. *Chem. Phys.* **1988**, *123*, 1.

(24) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(25) Ahlrichs, R.; Wär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 3.

(26) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Raghavachari, H. B. S. K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian Inc.; Pittsburgh, PA, 1990.

(27) Jensen, H. J. Aa.; Ågren, H. A. *Motecc-90*; IBM Corporation: Kingston, 1990.

(28) Stewart, J. J. P. *QCPE Bull.* **1985**, *5*, 133.

(29) Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1413.

(30) (a) Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1974**, *35*, 33. (b) Buenker, R. J.; Peyerimhoff, S. D. *New Horizons of Quantum Chemistry*; Reidel: Dordrecht, 1983.

(31) Langhoff, S. R.; Davidson, S. R. Int. *J. Quant. Chem.* **1974**, *81*, 61.

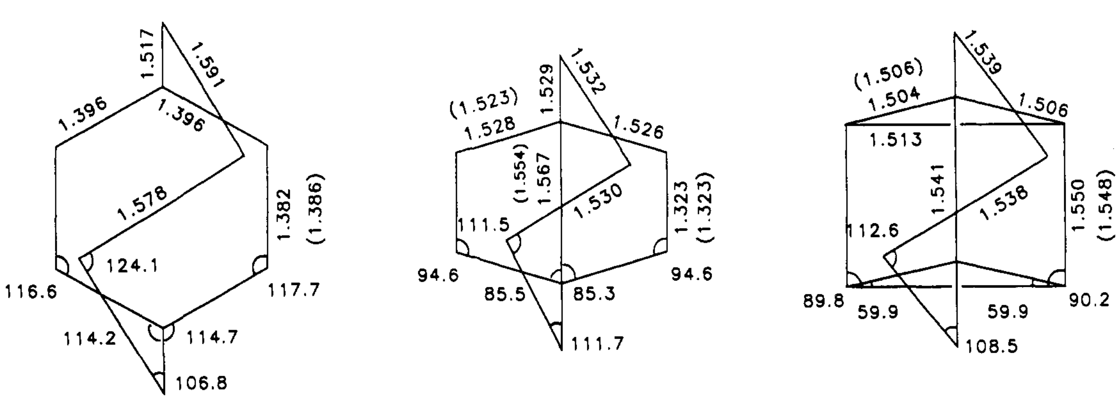


Figure 2. SCF optimized geometries (DZP basis set) of [4]paracyclophane and the Dewar benzene and prismane valence isomers. Bond lengths are given in angstroms, bond angles in degrees. The data given in parentheses refer to the parent molecules benzene (D_{6h}), Dewar benzene (C_{2v}), and prismane (D_{3h}).

0.3° in the various calculations. Thus it is concluded that valence double-ζ basis sets without polarization functions are sufficient for describing the geometries (but not the energy differences, see the following section) at the SCF level. The results of the SCF-DZP optimizations are summarized in Figure 2 and Table II. For comparison the data of the compounds with $n = 5$ and $n = 6$ from ref 18 and those of the parent compounds benzene, Dewar benzene and prismane are also contained in Table II.

The deformation angles α^{32} and β give a measure of the degree to which the benzene ring is bent as illustrated in Figure 1. The bond distance r_1 between the para ring carbon atoms is also important since it describes the movement of the benzene isomer on a "reaction coordinate" to the Dewar benzene isomer. It is obvious from Table II that the shortening of the $(CH_2)_n$ chain increases α and β monotonically ($\approx$5 and $\approx$10° per CH_2 group, respectively in the n = 6–4 series) and decreases the bond lengths r_1 and r_2. In [4]paracyclophane a significant amount of "strain" is also placed on the $(CH_2)_4$ chain as can be seen from the large C6–C6′ and C5–C6 bond distances (1.578 and 1.591 Å) and the very large C5C6C6′ bending angle of 124°. These values are (contrary to the deformation angles) very similar in the $n = 5$ compound (1.588 Å, 1.590 Å, and 121°, double-ζ basis set calculation[5]).

The bond alternation in the benzene ring of **1** is $\Delta r = 0.014$ Å at the DZP level ($\Delta r = 0.034$ Å (MNDO), 0.027 Å (STO-3G)[19]) with carbon–carbon distances ranging from 1.382 to 1.396 Å. The comparison of the calculated Δr values in the n = 4–7 compounds ($\Delta r = 0.014$ Å ($n = 4$); 0.025 Å ($n = 5$); 0.007 Å ($n = 6$), 0.009 Å ($n = 7$)[22]) shows that there is an even–odd alternation with respect to the degree of bond alternation in the [n]paracyclophanes (the values of the odd forms are larger). Thus the lower value of the [4]paracyclophane molecule relative to [5]paracyclophane cannot be interpreted with an increased "aromatic" character of the former compound.

The comparison of the present structural data (DZP basis set) with previous MNDO and STO-3G results[19] shows that both methods predict only slightly different values for the bond lengths and bond angles of [4]paracyclophane (the bond lengths are generally larger).

The $n = 4$ Dewar benzene and prismane forms, on the other hand, exhibit "normal" C–C bond distances in the chain around 1.53 Å. The geometries of the C_6H_4 skeletons of both isomers show only minor differences compared to the parent molecules Dewar benzene and prismane (see Figure 2). The geometries of **2** and **3** are nearly unaffected by shortening the $(CH_2)_n$ chain as was concluded previously for the Dewar benzene compounds with n = 7, 6, and 5.[15,18] The geometry of the Dewar benzene skeleton of **2** is slightly closer to that of the parent molecule as compared with the geometries of the $n = 5$ and $n = 6$ compounds[18] due to the strainless six-membered ring present in **2**.

Table III. Calculated Energy Differences (ΔE^a) of [4]Paracyclophane (**1**) and the Dewar Benzene Isomer (**2**) (Isomerization Energies) as Obtained from Various AO Basis Set Employing the SCF and MP2 Treatments

AO basis	ΔE_{SCF} (kcal/mol)	$\Delta E_{MP2}{}^b$ (kcal/mol)	E_{corr} (**1**) (au)	E_{corr} (**2**) (au)	ΔE_{corr} (kcal/mol)
6-31G	−9.4	2.2	−0.9140	−0.8955	11.6
DZ+d	−18.6	−3.6	−1.3023	−1.2784	15.0
DZP	−18.9	−3.4	−1.3889	−1.3642	15.5
TZP^c	−18.2	−3.1	−1.6329	−1.6089	15.1
TZ2P^c	−18.5				
TZP+f^c	−17.6				

[a] ΔE refers to the isomerization energy at the SCF and MP2 levels. E_{corr} is the amount of correlation energy accounted for with the MP2 treatment. ΔE_{corr} is the correlation energy difference between [4]-paracyclophane (**1**) and the corresponding Dewar benzene isomer (**2**). The total energies of **2** calculated with the basis sets given above are −385.377 84, −385.494 97, −385.525 54, −385.626 96, −385.640 58 and −385.636 23 au, respectively. [b] The MP2 calculations were performed at the SCF-optimized geometries with frozen carbon 1s MOs. [c] Single point calculations employing the SCF-DZP optimized geometry.

The MNDOC optimized geometries of the three molecules are generally very similar compared with the results of the DZP calculations; the deviations in bond length (bond angles) are generally less than 0.02 Å (2°). The largest differences are observed for the deformation angles α and β. Compared to the DZP values (29.7 and 38.2°) the MNDOC method tends to increase α (35.7°) at the expense of β (32.9°) which indicates a detailed energetic balance between the bending of the aromatic ring and the benzylic C–C bond. Similar observations have also been reported for the comparison of MNDO and STO-3G geometries of [4]paracyclophane.[19] The overestimation of the deformation angle α in [n]paracyclophanes (n = 7–5 ref 18 and references therein) seems to be a common failure of semiempirical MO and force field methods.

B. Isomerization and Strain Energies. To determine meaningful results for the energy differences between the three valence isomers at the SCF level a wide range of different basis sets was employed. The calculations with basis sets larger than DZP were carried out with the DZP optimized structures. The results are collected in Tables III and IV. The zero-point energies of the three isomers, as calculated with the 6-31G basis set, are equal to within 0.1 kcal/mol and thus have a negligible effect on the calculated isomerization energies.

Inspection of Table III shows that the energy difference between the benzene and Dewar benzene form ($\Delta E_{SCF} = E_{Dewarbz} - E_{benzene}$) decreases significantly by adding one set of polarization functions to the basis set of the carbon atoms (6-31G vs DZ+d). However, the ΔE values calculated with the DZ+d, DZP, TZP, TZ2P, and TZP+f basis sets are very similar, and thus it can be assumed that the energy difference between the potential minima of the $n = 4$ benzene and Dewar benzene isomer is ≈ -18 kcal/mol near

---

[32] The deformation angle α is not unambigously defined for the compounds with C_2 symmetry. However, the calculated geometries of the six-membered rings deviate only slightly from C_{2v} symmetry. Thus the values given in Table II were obtained by averaging the two slightly different deformation angles ($\Delta\alpha < 2°$) obtained from both sides of the molecule.

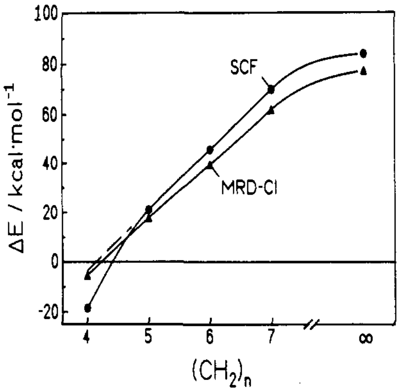


Figure 3. Energy differences between the [n]paracyclophane molecules and the corresponding Dewar benzene isomers as a function of the chain length n calculated with the SCF and MRD-CI method. The MRD-CI values were obtained with the model compounds **1b** and **2b**. The data of the $n = \infty$ (benzene and Dewar benzene) and the n = 7–5 compounds are taken from ref 18. The dashed line indicates the extrapolation of the SCF values to n = 4.

Table IV. Calculated Energy Differences (ΔE^a) of the n = 4 Dewar Benzene Form (**2**) and the Prismane Isomer (**3**) (Isomerization Energies) as Obtained from Various AO Basis Sets Employing the SCF and MP2 Treatment

AO basis	ΔE_{SCF} (kcal/mol)	$\Delta E_{MP2}{}^b$ (kcal/mol)	E_{corr} (3) (au)	ΔE_{corr} (kcal/mol)
6-31G	47.8	56.0	−0.8823	+8.3
DZ+d	39.3	38.1	−1.2804	−1.2
DZP	39.2	38.0	−1.3660	−1.1
TZP^c	40.9	40.2	−1.6100	−0.7
TZ2P^c	41.4			
TZP+f^c	40.0			

^{a} ΔE refers to the isomerization energy at the SCF and MP2 level. E_{corr} is the amount of correlation energy accounted for with the MP2 treatment. ΔE_{corr} is the correlation energy difference between Dewar benzene and prismane forms **2** and **3**. ^{b} The MP2 calculations were performed at the SCF-optimized geometries with frozen carbon 1s MOs. ^{c} Single point calculations employing the SCF-DZP optimized geometry.

the Hartree–Fock limit. This value is ≈15 kcal/mol lower than predicted by extrapolation of the n = 7, 6, and 5 series.[18] This is illustrated in Figure 3 with the calculated ΔE values of the $n = \infty$ (benzene and Dewar benzene) and the n = 7–4 compounds obtained from the SCF and MRD-CI (see below) treatments. The difference of the ΔE values with respect to both methods decrease steadily as n decreases. A clear variation is seen at n = 4 where the correlation energy correction becomes larger in the benzene form. This demonstrates that the breakpoint for the stability difference between the two isomers is identified with a significant change in the electronic structure of **1**. The validity of the SCF approximation for these molecules depends strongly on the chain length n, and thus correlation energy treatments are necessary to obtain reliable ΔE values.

The energy differences between the Dewar benzene compound (**2**) and the corresponding prismane isomer (see Table IV) exhibit a similar basis set dependence at the SCF level as discussed above. The polarization functions are mainly necessary to describe the energetic situation in the highly strained benzene and prismane forms. The isomerization energy for the [$2_\pi + 2_\pi$] cycloaddition reaction of the Dewar benzene to the prismane form is calculated to be ≈40 kcal/mol at the SCF level. Contrary to the former reaction this value is similar to the calculated energy difference between the unsubstituted parent molecules Dewar benzene and prismane (ΔE_{SCF} = 39 kcal/mol, DZ + d basis set). The photochemical conversion of the Dewar benzene-type molecules in their lowest excited singlet and triplet states ($E(S_1) \approx 100$ kcal/mol, $E(T_1) \approx 70$ kcal/mol[33]) to the prismane forms is strongly exothermic (≈-30–60 kcal/mol), even in the case of the n = 4 compound which explains the formation of **3** in the photolysis of **2** as a side product.[9]

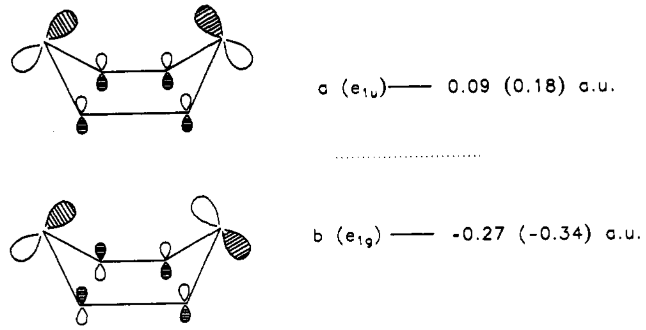


Figure 4. Schematic description of the HOMO and LUMO of [4]-paracyclophane. Symmetry symbols and the orbital energies in parentheses refer to the benzene molecule for comparison. The "bending" of the p_z orbitals at the bridgehead positions is deduced from the large contributions of the carbon p_x AOs ($|c_{px}| = 0.13$, $|c_{pz}| = 0.46$) to the HOMO and LUMO MO vectors.

To obtain an initial guess for the correlation energy contribution of the isomerization energies, single point MP2 calculations have been carried out with basis sets up to TZP quality. The results as presented in Tables III and IV clearly show that the MP2 energy corrections are generally larger in the benzene than in the Dewar benzene or prismane forms. While the SCF energy difference is already converged, the MP2 energy corrections show a small basis set dependence. Expansion of the basis set slightly favors the form with larger correlation energy, an effect which is known for isomers with different electronic structure.[34] For the **1** → **2** isomerization energy ΔE_{MP2} a value around −3 kcal/mol can be regarded as correct. This result contradicts prior experience with the n = 7, 6, and 5 molecules in which the correlation energy corrections are larger for the Dewar benzene form.[18] The indicates that [4]paracyclophane could be classified as the borderline case between strained "closed shell" type ($n > 4$) and diradical-like molecules ($n < 5$). The diradicaloid nature[35] of the [4]paracyclophane molecule is also demonstrated by inspection of the orbital occupation numbers obtained from the CAS-SCF wave function (eight electrons distributed in eight MOs, DZ + d basis set). The highest occupied MO (HOMO) of b-symmetry (which corresponds to one of the e_{1g} MOs of benzene) formally has a deficiency of 0.23 electrons which are "moved" (by double excitations) mainly into the lowest unoccupied MO (LUMO) of a-symmetry (e_{2u} of benzene). Since both MOs are essentially centered at the bridgehead positions (see Figure 4), this analysis easily explains the observed reactivity of **1** against nucleophilic attack at these carbon atoms.[9,13]

Considering the situation discussed above one can ask about the validity of the SCF geometry optimizations of **1**. Due to the size of the molecules, semiempirical MNDOC optimizations were performed including the MP2 corrections in the energy gradient evaluation. The difference between the isomerization energy as obtained with the MP2 optimized and the MP2 single point (SCF geometries) calculations is only −0.2 kcal/mol[36] which demonstrates the applicability of the SCF optimized geometries.

The MP2 energy contributions to the **2** → **3** isomerization energy also increase the stability of the more strained prismane form but are generally small (≈−1 kcal/mol) for the larger basis sets.

From the calculated energy differences with respect to the Dewar benzene form and the structures presented so far, it is evident that [4]paracyclophane and the prismane valence isomer are highly strained molecules. To gain some more insight into

---

[33] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings: Menlo Park, CA, 1978.

[34] Parasuk, V.; Almlöf, J. *J. Chem. Phys.* **1991**, *94*, 8172.

[35] For a definition of the term "diradicaloid" see, for example: Salem, L.; Rowland, C. *Angew. Chem.* **1972**, *84*, 86.

[36] The ΔE_{SCF} (ΔE_{MP2}) value calculated with the MNDOC method is −23.8 (−16.8) kcal/mol.

Table V. Partial and Total Strain Energies SE (in kcal/mol) of the C_6H_4 Skeleton and the $(CH_2)_4$ Chain in Compounds **1**–**3**[b]

compound	method[a]	$SE_{C_6H_6}$	SE_{CHAIN}	SE_{TOT}
benzene form (**1**)	SCF	95.5	12.1	107.6
benzene form (**1**)	MP2	79.4	11.9	91.3
Dewar benzene form (**2**)	SCF	0.4	2.1	2.5
Dewar benzene form (**2**)	MP2	0.2	1.4	1.6
prismane form (**3**)	SCF	3.5	2.5	6.0
prismane form (**3**)	MP2	3.2	1.8	4.0

[a] DZP basis set. The carbon 1s MOs were frozen in the MP2 calculations. [b] For a description of the computational details see text.

Table VI. Isomerization Energies ΔE and Correlation Energy Contributions E_{corr} of [4]Paracyclophane (**1**) and the Corresponding Dewar Benzene Isomer (**2**) Obtained by Treating the C_6H_6 Skeleton in the Cyclophane Geometry[d]

method[a]	E_{corr} (**1b**) (au)	E_{corr} (**2b**) (au)	ΔE_{corr} (kcal/mol)	ΔE (kcal/mol)
SCF				−18.5
MP2, 1s in core[b]	−0.7722	−0.7567	9.7	−9.8
MP4SDTQ, 1s in core[b]	−0.8474	−0.8314	10.1	−8.4
CAS-SCF, 8e in 8 MOs	−0.1008	−0.0833	11.0	−7.4
CAS-SCF, 12e in 12 MOs	−0.1528	−0.1328	12.5	−5.9
MRD-CI, 20e[c]	−0.4778	−0.4573	12.9	−5.6

[a] DZ+d basis set (102 contracted basis functions). [b] 30e correlated in 96 MOs. [c] MOs with $\epsilon < -0.75$ and $\epsilon > 10$ au in core (85 MOs). [d] The added SCF energy contribution of the $(CH_2)_4$ chain as obtained by calculating the butane molecule in the chain geometries of **1** and **2** is −10.0 kcal/mol at the DZ+d level.

this point, an energy partitioning into the so-called strain energies was performed which has already been useful in the description of [*n*]paracyclophanes.[5,15,19,20] The strain energy (SE) of the C_6H_6 skeleton is defined by the following calculational procedure: the $(CH_2)_4$ chain is formally removed, freezing the benzene, Dewar benzene, or prismane skeleton in the present conformation and placing two additional hydrogen atoms at a typical C–H distance in the same direction as the first carbon atoms of the chain. The energy difference between this structure (**1b**, **2b**, and **3b**, respectively) and the parent molecule itself (benzene, Dewar benzene, and prismane, optimized with the same basis set) gives a measure of the strain energy $SE_{C_6H_6}$. The analogous caculational procedure with the $(CH_2)_4$ chain and the butane molecule (gauche conformation) as a reference results in SE_{chain}. The data presented in Table V can be summarized as follows: The total strain energy of [4]paracyclophane as evaluated at the MP2/DZP level (91 kcal/mol) by far exceeds the resonance energy of benzene (20–40 kcal/mol[37] and references therein). The SE_{TOT} value is in good agreement with the MNDO estimation (SE_{TOT} = 88 kcal/mol) of Jenneskens et al.[19] The corresponding value obtained with the STO-3G basis set (SCF: 126 kcal/mol[19]) is certainly an overestimate due to the inflexibility of the wave function used. The largest energy contribution (87%) arises from the deformation of the benzene skeleton. However, the contribution of the chain to SE_{TOT} of **1** is significantly higher than in the corresponding Dewar benzene and prismane forms which corroborates the qualitative predictions of the geometry analysis in the preceding section.

The next question is, whether the MP2 treatment is sufficient to account for the correlation energy contribution to the **1** → **2** isomerization energy. Due to the diradicaloid nature of the [4]paracylophane molecule this problem seems to be more important in the *n* = 4 compounds than in the *n* = 7–5 series.[18] Therefore, a number of correlation treatments were undertaken, as summarized in Table VI. Due to the size of the molecules these treatments are only feasible with the benzene (**1b**) and Dewar benzene (**2b**) type molecules frozen in the respective cyclophane geometry as used in the strain energy calculations (see above). The prismane isomer is omitted from this analysis due to the applicability of the SCF approximation for this molecule.

Table VII. Calculated Energy Differences (ΔE in kcal/mol) of [4]Paracyclophane (**1**) and the Corresponding Dewar Benzene Isomer (**2**) (Isomerization Energies) Obtained with MINDO/3, MNDO, MNDOC, and AM1 Semiempirical Methods[d]

method	ΔE_{SCF} **1** → **2**	ΔH_f[a] cyclobutene	ΔE_{SCF} corrected
MNDO/3	−7.3	33.0 (−4.5)	1.7
MNDO	−17.5	31.0 (−6.5)	−4.5
MNDOC	−23.8	29.7 (−7.8)[b]	−8.2[c]
AM1	14.1	45.8 (8.3)	2.5

[a] The experimental value is 37.5 kcal/mol.[48] [b] Including BWEN-perturbation theory correction.[29] [c] The MP2 energy correction appropriate to the MNDOC treatment yields a corrected ΔE value of −1.2 kcal/mol. [d] Two times the error in ΔH_f of the cyclobutene molecule (in parentheses) is added to the ΔE_{SCF} value to obtain the corrected energy difference.

Table VI shows that the approximated isomerization energy at the SCF level (−18.5 kcal/mol) corresponds rather nicely with the value obtained by the full calculation of **1** and **2** (−18.6 kcal/mol). However, the correlation energy correction ΔE_{corr} of the MP2 treatment obtained for the transformation **1b** → **2b** is 5.3 kcal/mol smaller than calculated for the molecules containing the chain. This difference demonstrates the importance of substituents (CH_2 vs H) at the bridgehead positions for the ΔE_{corr} corrections.[38] Keeping this in mind, the ΔE_{corr} values obtained from the different calculational methods are only estimates of the "true" correlation energy difference of **1** and **2**.

Generally it is seen that the relative stability of the benzene form increases with the application of more sophisticated correlation treatments (MP4SDTQ vs MP2, CAS-SCF: 12e vs 8e correlated). However the small difference between the MP2 and MP4SDTQ values (1.4 kcal/mol) shows that double excitations predominate in the ΔE_{corr} corrections. Theoretically the CAS-SCF method effectively introduces near-degeneracy effects, while the MRD-CI approach additionally accounts for the effects of higher excited reference configurations with respect to the Hartree–Fock determinant. Indeed both methods yield larger ΔE_{corr} values than the MPn treatments, but the energetic influence of the effects stated above seems to be small. The weight of the HF determinant in the CAS-SCF wave function of **1b** is 81% which is ≈10% lower than for the Dewar benzene isomer **2b**. Thus it is concluded that **1** is a borderline case for the applicability of single-reference determinant approaches. Furthermore, it should also be noted that the CAS-SCF treatment including only the six π electrons of the benzene moiety yields a negative ΔE_{corr} correction which emphasizes the importance of σ–π correlation effects in these systems.

Assuming that the ΔE_{corr} values calculated for the **1b** → **2b** system are ≈5–6 kcal/mol lower due to the missing $(CH_2)_4$ chain, we can estimate from the MRD-CI value (ΔE = −5.6 kcal/mol) a final isomerization energy of 0 ± 3 kcal/mol for the reaction **1** → **2**. The estimated error limits contain the ΔE_{MP2} values (≈−3 kcal/mol) obtained from the full calculation of **1** and **2**. Although the estimated ΔE value is somewhat uncertain (note however the size and the complexity of the investigated molecules) it seems clear that the *n* = 4 paracyclophane molecule is the breakpoint for the stability difference between the benzene and Dewar benzene form in the *n* = 6–4 series. This result contradicts semiempirical investigations of the *n* = 10–4 compounds using MINDO/3,[39] MNDO,[40] and AM1[41] Hamiltonians which place the *n* = 4 Dewar benzene form energetically -20–25 kcal/mol

---

(37) George, P.; Bock, C. W.; Trachtman, M. *Tetrahedron Lett.* **1985**, *26*, 5667.

(38) An estimation of the basis set superposition error (BSSE) introduced by the splitting of the [4]paracyclophane molecule into the ring and the chain yields a small value of 1.5 kcal/mol at the SCF + MP2 level. The BSSE corrected ΔE_{MP2} value for the **1b** → **2b** transformation is −8.3 kcal/mol.

(39) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(40) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(41) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

Table VIII. Comparison of Calculated (MRD-CI, DZ+d Basis Set[a]) and Experimental Vertical Excitation Energies (in eV) for [4]Paracyclophane (**1**), Benzene in the Skeleton Geometry of **1** (**1b**) and Benzene

state	sym[b]	**1b** (calc)	**1** (exptl[c])	benzene (calc)	benzene (exptl)
T_1	$1B/B_{1u}$	2.6	1.9[c]	4.3	3.7[e]
S_1	$2B/B_{2u}$	3.4	3.4–3.2[d]	5.3	4.9[f]
S_2	$1A/E_{2g}$	4.3	3.8–3.6[d]	9.3	7.8[g]
S_3	$3B/B_{1u}$	4.8	4.8[d]	7.1	6.2[g]
S_4	$4B/E_{1u}$	5.9		8.3	7.0[g]

[a] 20e are correlated; MOs with $\epsilon < -0.75$ and $\epsilon > 10$ au in core (85 MOs). [b] The first symbol refers to the state of **1b** and **1**, the second to the states of benzene. [c] Estimated from the extrapolation of the T_1 state energies as a function of the deformation angle α of the (n = 10, 8, 7) [n]paracyclophane compounds as suggested by Hopf et al.[8] [d] Absorption maximum in ethanol at 77 K.[13] [e] Phosphorescence 0–0 transition in cyclohexane at 77 K.[49] [f] Absorption maximum in hexane solution at room temperature.[49] [g] Gas-phase value from ref 50.

below the benzene form and indicate a breakpoint at n = 5–6.[15] Since the various semiempirical methods yield very different values for the energy difference between the benzene and the Dewar forms, a correction with the measured reaction enthalpy of the hexamethylbenzene → (hexamethyl) Dewar benzene reaction (ΔH_R = 60 kcal/mol[42]) was applied.[15] Due to a significant influence of the methyl substituents on the isomerization energy[18] this procedure seems inappropriate. Instead, a correction for the known errors of the semiempirical methods in the description of the cyclobutene moiety (see Table VII) present in the Dewar benzene forms yields satisfactory results as compared to the ab initio value of 0 ± 3 kcal/mol. The implicit inclusion of electron correlation in the semiempirical methods seems to describe the energetic situation in the strained [4]paracyclophane molecule accurately enough.

Unfortunately, no experimental isomerization enthalpies are available for comparison with the calculated data. However, the experimental results[9,13] suggest that the [4]paracyclophane molecule is stable against a thermal back reaction to the Dewar form (instead polymerization and a bimolecular addition of the solvent are observed). This result seems compatible with the present estimation of ΔE since in the case of large negative ΔE values (<–20 kcal/mol) the [4]paracyclophane molecule is energetically situated above the barrier for the thermal back reaction of the Dewar form (E_a is generally around 20 kcal/mol, regardless of the chain length n[11,12]), which should result in a fast (but unobserved) back reaction to **2**.

C. Excited States. The electronic absorption spectrum recorded after the photolysis of the n = 4 Dewar benzene form (**2**) has given essential proof for the formation of the [4]paracyclophane molecule.[13] This spectrum shows two strong bands (relative intensity 2:1) centered at 260 and 340 nm. For the long wavelength absorption it has been suggested that it might consist of at least two components with maxima at 330–340 and 370–380 nm.[13] Compared to the n = 5 compound[4] this corresponds to a reasonable bathochromic shift for the $S_0 \rightarrow S_1$ transition of 40–50 nm. The calculational results for some of the low-energy states of **1** obtained from a MRD-CI treatment using the compound **1b** (without the chain) as a model system are presented in Table VIII. Additionally the analogous results for the parent molecule benzene are also collected to demonstrate the error limits of the calculated state energies.

Generally the analysis of the MRD-CI wave function shows that all calculated states can be interpreted as perturbed benzene-type excited states. All calculated state energies are significantly lower compared to the parent molecule benzene which is mainly attributable to the reduced HOMO–LUMO energy gap (9.8 vs 14.2 eV). The agreement of the calculated state energies with respect to the experimental values is quite good. However, it is noted that a partial cancellation of the errors occurs due to the neglected $(CH_2)_4$ chain (this effect is ±0.5 eV as estimated from MNDOC-SDCI calculations of **1**) and the poor AO basis. The last effect is seen by comparison of the calculated and experimetal values for the excited states of the benzene molecule which show an energetic overestimation of 0.5–0.9 eV for the three lowest states.

The T_1 state (1^3B of **1b**) of **1** is interpreted to be mainly of B_{1u} character with a dominant contribution (85%) from the HOMO → LUMO singly excited configuration. The calculated red shift with respect to the benzene molecule (1.7 eV) corresponds quite well to the experimental value of 1.8 eV. The two strong absorption bands in the UV spectrum of **1** (3.2–3.8 and 4.8 eV) are assigned as ${}^1A_{1g} \rightarrow {}^1B_{2u}$ and ${}^1A_{1g} \rightarrow {}^1B_{1u}$ type transitions (calculated oscillator strengths 0.17 and 0.73, respectively). The second excited singlet state (2^1A) arises mainly from a double excitation HOMO → LUMO and is assigned as a perturbed benzene-like E_{2g} state. This state shows the largest red shift as compared to the benzene molecule (calc 5 eV, exptl ≈ 4 eV) which is explained by the partial diradicaloid character of the [4]paracyclophane molecule. In view of the low calculated oscillator strength for the transition to the E_{2g} type state ($f = 6 \times 10^{-4}$), the origin of the second band (underlying the band at 3.2–3.8 eV) in the experimental spectrum of **1** seems unclear. Furthermore, a strong red shift of this one band (0.4–0.5 eV) is observed for the ring substituted compound with R = CO_2Me. Attempts to calculate this substituent effect with the MNDOC-SDCI method yield a much lower shift around 0.1 eV. Due to both discrepancies the observed shift may also be attributed to a strong solvent effect or an impurity with a high exctinction coefficient, but a conclusive decision on the basis of the calculational results does not seem possible. In summary, it is concluded that the assignment of the main parts of the experimental UV spectrum to the absorptions of the [4]paracyclophane molecule is correct.

IV. Conclusions

Most of the calculational results suggest that the [4]paracyclophane molecule is best classified as a strained organic molecule with partial diradicaloid character. The requirement of the matrix-isolation technique used in the preparation of **1**[13] supports this suggestion from a chemical point of view. On the basis of the theoretical results this is mainly demonstrated by the failure of the Hartree-Fock approximation in the description of the relative energy of **1**. Correlation energy corrections based on single-reference determinant treatments (MP2, MP4SDTQ) can account for most of the correlation energy difference between the n = 4 benzene and Dewar benzene isomers. The strain energy calculations show that **1** may be judged to be nonaromatic. However, the small degree of the bond alternation in the distorted benzene ring and the benzene-type excited states shows that some benzene-like character is retained due to the topology of the carbon skeleton.

Acknowledgment. The services and computer time made available by the Sonderforschungsbereich (SFB) 334 have been essential to the study. This work was financially supported by the Deutsche Forschungsgemeinschaft through the Leibniz Prize of S. D. Peyerimhoff. I wish to thank S. D. Peyerimhoff for supporting this work and for fruitful comments and discussions. I also thank B. A. Hess for his help with some of the programs used and B. Engels for helpful comments.

---

(42) Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 646.

(43) Hehre, W. J.; Ditchfeld, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(44) Poirier, R.; Kari, R.; Csizmadia, I. G. *Handbook of Gaussian Basis Sets*; Physical Sciences Data 24, Elsevier: Amsterdam, 1985.

(45) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(46) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(47) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 5059.

(48) Turner, R. B.; Goebel, P.; Mallon, B. J.; Doering, W. von E.; Coburn, J. F., Jr.; Pomerantz, M *J. Am. Chem. Soc.* **1968**, *90*, 4315.

(49) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.

(50) Nakashima, N.; Yoshihara, M. S. K. *J. Chem. Phys.* **1980**, *73*, 5976.