

## Pentalene: Formation, Electronic, and Vibrational Structure

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**Abstract:** Pentalene (**1**) is generated for the first time in argon matrices by photocleavage of the corresponding dimer (**2**). It is found that the cleavage occurs in two distinct steps, the first of which leads presumably to a diradical. **1** is characterized by its electronic and vibrational absorption spectra which are assigned and interpreted with reference to different quantum chemical calculations. These show that the first two excited states of pentalene involve a doubly excited configuration which had been ignored in previous discussion of the electronic structure. Due to the antiaromatic nature of pentalene, the distortive force of the  $\pi$ -electrons which favor a  $C_{2h}$  structure with localized single and double bonds predominates over the effect of the  $\sigma$ -electrons which drive the molecule to a  $D_{2h}$  structure.

## 1. Introduction

Pentalene (**1**) has fascinated synthetic as well as physical and theoretical organic chemists for more than four decades.<sup>1</sup> In spite of this, convincing spectroscopic evidence for the parent system is still missing. So far, all pentalene derivatives which have been characterized or isolated were either sterically shielded or electronically stabilized. Thus, hexaphenylpentalene was the first simple pentalene which was isolated in 1962 by Le Goff,<sup>2</sup> whereas push–pull substituted pentalenes such as 1,3-bis(dimethylamino)pentalene<sup>3a</sup> or 1,4-diamino-3,6-dimethylpentalene-2,5-dicarbonitrile<sup>3b</sup> did not allow unambiguous conclusions with regard to the properties of the electronically unperturbed system.

In the 1970's experimental evidence for thermally unstable alkylpentalenes began to appear, starting with the trapping and UV characterization of 1-methyl-,<sup>4a,b</sup> 2-methyl-, and 1,3-dimethylpentalene,<sup>4b</sup> and culminating with the successful isolation<sup>4c</sup> and spectroscopic<sup>4c,d</sup> as well as structural characterization<sup>4e</sup> of 1,3,5-tri-*tert*-butylpentalene which was recently re-subjected to detailed scrutiny by electronic and vibrational spectroscopy.<sup>5</sup> Thermally induced  $8\pi$  cyclization of 8-[(di-alkylamino)vinyl]fulvenes proved to be a very useful synthetic route to pentalenes,<sup>6</sup> which also led to the isolation of the parent pentalene dimer (**2**) and cycloaddition products with cyclopentadiene in cases where pentalene **1** was formed as a reactive intermediate.<sup>4b</sup>

Parent pentalene has been the subject of numerous Hückel-type or semiempirical theoretical studies which focussed primarily on the reason for and the extent of the bond alternation in this formally antiaromatic species<sup>7</sup> or on its excitation energies.<sup>7b,d</sup> Surprisingly, the literature records only a single *ab initio* study on **1** which focussed on the automerization reaction. There, 4-31G/STO-3G SCF calculations predicted a barrier of  $\approx 14$  kcal/mol for the automerization process.<sup>8</sup> Very recently, Schleyer and Jiao predicted a pronounced exaltation of the magnetic susceptibility of pentalene<sup>9</sup> due to the paramagnetic ring current of its  $8\pi$  electron system, in concordance with earlier NMR findings on tri-*tert*-butylpentalene.<sup>4c</sup>

Very recently we found two straightforward synthetic pathways to pentalene dimers **2** and **3**, starting with the dihydropentalene **4**:<sup>11</sup> Whereas the bromination/dehydrobromination series **4**  $\rightarrow$  **5**  $\rightarrow$  **1** yields exclusively the *syn-cis* dimer **2** (besides polymers and byproducts), twofold deprotonation **4**  $\rightarrow$  **6** and CuCl<sub>2</sub> induced oxidative coupling of pentalene dianion **6** gives a diastereomeric mixture of **2** and **3** (Scheme 1).<sup>11</sup> Although the yields are very moderate in both cases (path A:  $\approx 15\%$ ; path B:  $\approx 12\%$ ), pure samples of crystalline pentalene dimers **2** and **3** are easily accessible by simple “one-pot” reactions. Similar to the dimers of methylpentalenes,<sup>4a,b</sup> **2** and **3** undergo photochemical [2 + 2] and thermal [8 + 2] cycloreversions. The present paper reports on the results of photocleavage experiments of **2** in argon matrices and on accompanying quantum chemical calculations on the molecular, electronic, and vibrational structure of pentalene **1**.

(7) See, for example: (a) Binsch, G.; Heilbronner, E.; Murrell, J. N. *Mol. Phys.* **1966**, *11*, 305. (b) Nakajima, T. *Top. Curr. Chem.* **1972**, *32*, 1. (c) Koyanagi, T.; Yamaguchi, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 521. (d) Baird, N. C.; West, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 3072. For some more recent work in this vein, see Ref 5 or: (e) Boehm, M. C.; Schütt, J. *J. Phys. Chem.* **1992**, *96*, 3674.

(8) Jean, Y. *Nouv. J. Chim.* **1980**, *4*, 11. A remarkable finding of this study was that, at the STO/3G level, the lowest singlet state of  $D_{2h}$  symmetry (which should represent the transition state for the rapid automerization of the  $C_{2h}$  structures) is an *open-shell* state 2.1 kcal/mol below the closed-shell singlet. Although this ordering was reversed at the 4-31G level, it would be interesting to see what state-of-the-art *ab-initio* calculations have to say about the ordering of states in  $D_{2h}$  pentalene (cf. ref 22).

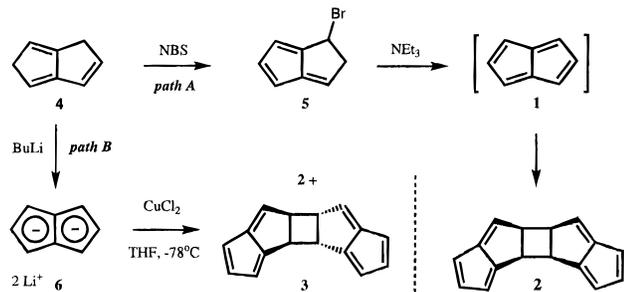
(9) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.

(10) Meier, H.; Pauli, A.; Kochhan, P. *Synthesis* **1987**, 573. Meier, H.; Pauli, A.; Kolshorn, H.; Kochhan, P. *Chem. Ber.* **1987**, *120*, 1607.

(11) You, S.; Neuenschwander, M. *Chimia* **1996**, *50*, 24.

<sup>†</sup> University of Fribourg.<sup>‡</sup> University of Bern.<sup>§</sup> Present address: Department of Chemistry, University of Alberta, Edmonton, Canada.<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, February 1, 1997.(1) For a survey of the literature, see e.g.: Lindner, H. J. Pentalene und Dihydropentalene. In *Houben-Weyl*; Georg Thieme: Stuttgart, 1985; Vol 5/2c, p 103 ff.(2) Le Goff, E. *J. Am. Chem. Soc.* **1962**, *84*, 3935.(3) (a) Hafner, K.; Bangert, K. F.; Orfanos, V. *Angew. Chem.* **1967**, *79*, 414. (b) Hartke, K.; Matusch, R. *Chem. Ber.* **1972**, *105*, 2584.(4) (a) Bloch, R.; Marty, R. A.; de Mayo, P. *J. Am. Chem. Soc.* **1971**, *85*, 362. Block, R.; Marty, R. A.; de Mayo, P. *Bull. Soc. Chim. Fr.* **1972**, 2031. (b) Hafner, K.; Dönges, R.; Goedecke, E.; Kaiser, R. *Angew. Chem.* **1973**, *85*, 362; *Int. Ed. Engl.* **1973**, *12*, 337. (c) Hafner, K.; Süß, H. U. *Angew. Chem.* **1973**, *85*, 626; *Int. Ed. Engl.* **1973**, *12*, 575. (d) Bischof, P.; Gleiter, R.; Hafner, K.; Knauer, K. H.; Spanget-Larsen, J.; Süß, H. U. *Chem. Ber.* **1978**, *111*, 932. (e) Kitschke, B.; Lindner, H. J. *Tetrahedron Lett.* **1977**, 2511.(5) Falchi, A.; Gellini, C.; Salvi, P. R.; Hafner, K. *J. Phys. Chem.* **1995**, *99*, 14659.(6) Kaiser, R.; Hafner, K. *Angew. Chem.* **1973**, *85*, 361; *Int. Ed. Engl.* **1973**, *12*, 336.

## Scheme 1



## 2. Methods

**1. Synthesis.** The syntheses of the pentalene dimers were described in a recent report.<sup>11</sup> For the purposes of the presently described experiments we used exclusively the *syn-cis* dimer as<sup>2</sup> obtained by the bromination/dehydrobromination route (path A in the Scheme 1).

**2. Matrix Isolation and Spectroscopy.** Ground crystals of the pentalene dimer precursor were placed in a U-shaped tube immersed into a water bath and connected to the inlet system of a closed-cycle cryostat. While the bath was kept at  $25^\circ\text{C}$ , a 2:3 mixture of nitrogen and argon flowing through the tube at a rate of  $\approx 1$  mmol/h swept the precursor along onto a CsI window held at  $\approx 20$  K. There the mixture accumulated to form a matrix containing a sufficient quantity of the dimer within 2 h (the nitrogen was only added to improve the optical quality of the matrices such as to permit easier recording of UV spectra; for reasons of simplicity we will continue to call these "argon matrices" in the text).

After taking reference spectra, the cryostat was immersed into a merry-go-round array of low-pressure Hg lamps where it was exposed to stepwise 254-nm irradiation. In some experiments, the 313-nm line of a medium-pressure Hg lamp was used to photolyze the intermediate which accumulated during the initial phases of the 254-nm irradiation. Annealing experiments after photocleavage yielded no indication of re-dimerization of pentalene which occurs, however, rapidly in Freon matrices after thawing at 80 K.

Electronic absorption (EA) spectra were taken between 190 and 1500 nm with a Perkin Elmer Lambda 19 instrument whereas IR spectra were obtained on a Bomem DA3 interferometer ( $1\text{ cm}^{-1}$  resolution) equipped with an MCT detector ( $500\text{--}4000\text{ cm}^{-1}$ ).

**3. Quantum Chemical Calculations.** The geometries of pentalene in  $D_{2h}$  and  $C_{2h}$  symmetry were optimized at the SCF and MP2 levels as well as by the BLYP and B3LYP density functional methods<sup>12</sup> as implemented in the Gaussian 94 suite of programs,<sup>13,14</sup> always using the 6-31G\* basis set. The same methods were also used to calculate harmonic force fields which were subsequently fed into a proprietary program for carrying out normal mode analyses and scaling force fields to fit vibrational spectra.<sup>15</sup>

Excited state calculations were carried out at the BLYP/6-31G\* geometries by the CASSCF/CASPT2 procedure<sup>16</sup> with the MOLCAS program.<sup>17</sup> For the calculation of the  $\pi$  excited states the active space

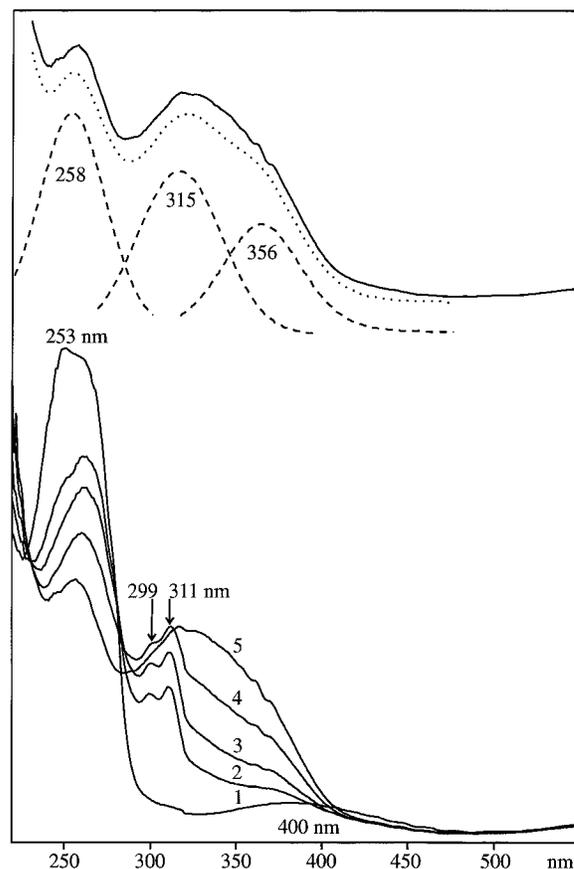
(12) (a) Becke, A. D. *Phys. Rev. A* **1988**, *39*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

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(14) For a description of the density functionals as implemented in the Gaussian series of programs, see: Johnson, B. G.; Gill, P. M. W. L.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.

(15) Tang, W.; Bally, T. J. *Phys. Chem.* **1993**, *97*, 4365.

(16) (a) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483. (b) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218. (c) Andersson, K.; Roos, B. O. In *Modern Electronic Structure Theory*; World Scientific Publishing: Singapore, 1995; Part 1, Vol 2, p 55.



**Figure 1.** Bottom: Stepwise conversion of the pentalene dimer (spectrum 1) via the intermediate (spectra 2–4) to pentalene (spectrum 5). Top: Deconvolution of spectrum 5 (solid) with three Gaussians (dashed) to give the dotted model spectrum.

comprised all 8  $\pi$ -electrons in 8  $\pi$ -MO's. In order to estimate the energies of the lowest states involving excitations from or to  $\sigma$ -MO's, the lowest and highest  $a_u$   $\pi$ -MO's were deleted from the active space and replaced by two sets of  $\sigma$ -MO's of  $a_g$  and  $b_u$  symmetry, resulting in a CAS(10,10) calculation. The  $\pi$  active space permitted evaluation of the lowest three states of  $A_g$  symmetry (including the ground state) as well as the lowest four of  $B_u$  symmetry, whereas with the (10,10) space the lowest two states of  $A_u$  and  $B_g$  symmetry could be calculated satisfactorily. Any attempt to calculate higher excited states of each symmetry resulted in severe problems with intruder states in the CASPT2 part whose remediation would have required an extension of the active space beyond the limits imposed by the program and hardware. Satisfactory agreement with experiment was obtained with the simple [C]3s2p1d/[H]2s ANO DZ basis set;<sup>18</sup> therefore we saw no necessity to add higher angular momentum and/or diffuse functions.

In an effort to provide a more transparent picture of the excited state electronic structure than can be obtained by CASSCF we performed additional CIS and CISD calculations based on ground state SCF MO's by the INDO/S method<sup>19a</sup> using the ZINDO program.<sup>19b</sup>

## 3. Results and Discussion

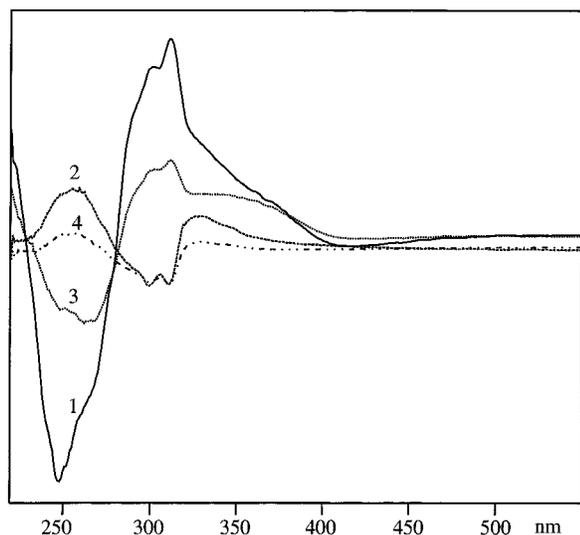
## 1. Formation and Electronic Absorption (EA) Spectrum.

Figure 1 shows the EA spectrum of the *syn-cis* dimer of pentalene **2** in argon (trace 1) which shows the expected fulvene-

(17) Molcas, Version 3: Andersson, K.; Blomberg, M. R. A.; Fülischer, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O.; University of Lund, Sweden, 1994.

(18) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

(19) (a) Zerner, M. C.; Ridley, J. E. *Theor. Chim. Acta* **1973**, *32*, 111. (b) Zerner, M. C.; Quantum Theory Project, University of Florida, Gainesville.



**Figure 2.** Difference spectra for the stepwise decomposition of the pentalene dimer: (1) after 15 min of 254-nm irradiation; (2) after subsequent 3 min of 313-nm irradiation; (3) after another 15 min of 254-nm irradiation; and (4) after 8 min of 313-nm irradiation.

type features (the strong UV and the weak near-UV band whose tail is responsible for the characteristic deep yellow color of this chromophore). Traces 2–5 show its stepwise conversion to pentalene which has a broad asymmetric band peaking at  $\approx 320$  nm and a sharper band with  $\lambda_{\text{max}} = 260$  nm,<sup>20</sup> i.e. a habitus which at first sight looks similar to that of the 1,3,5-tri-*tert*-butyl<sup>4d,5</sup> and the methyl<sup>4a</sup> or the 1,3-dimethyl derivative (where a conversion similar to that in Figure 1 was documented).<sup>4b</sup>

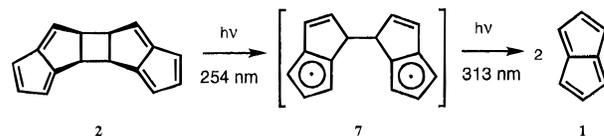
A closer scrutiny reveals, however, some marked differences. Firstly, we could see no trace of the transition which gives rise to a weak broad band around 600 nm in the spectra of 1,3,5-tri-*tert*-butylpentalene.<sup>4d,21</sup> Although this could be due to the fact that we are unable to generate sufficiently high concentrations of pentalene to reveal this transition, we note that it is not rigorously forbidden by symmetry in the above derivative which has only  $C_s$  symmetry whereas this is the case in the parent compound which has  $C_{2h}$  symmetry. Therefore this transition could only gain intensity through vibronic coupling which may be very weak. Furthermore, the anticipated strong geometry changes on  $S_0 \rightarrow S_1$  excitation<sup>5</sup> would cause the band to be very broad and hence even more difficult to detect.

Secondly, we are certain that the band at 260 nm is *not* due to residual dimer but to pentalene because it rises in concert with the near-UV and also with the IR bands which we attribute to pentalene (see below). A similar peak remained also after photolysis of the dimer of 1,3-dimethylpentalene<sup>4b</sup> and may give rise to the shoulder recorded in the onset of the strong far-UV transition of 1-methylpentalene.<sup>4a</sup> Conversely, the position of a corresponding band does not become apparent in the tri-*tert*-butyl derivative which could indicate the need for a reassignment of its spectrum as proposed below. Finally, we were unable to record the position of the intense band maximum below 230 nm which corresponds to the well-defined 215-nm peak in the spectrum of the tri-*tert*-butyl derivative. However, as our theoretical treatment did not permit an unambiguous assignment of excited states at such high energies, we did not pursue this matter.

(20) A referee has pointed out that this spectrum could possibly be perturbed due to the fact that two pentalene molecules are trapped in the same matrix cage. We cannot rule out this possibility but the effect appears to be weak enough that it does not stand in the way of a coherent assignment.

(21) We carefully checked all spectra up to 1500 nm but could find no unambiguous evidence for any band associated with the UV bands of pentalene.

## Scheme 2



**Table 1.** C–C Bond Lengths of Pentalene<sup>a</sup>

	HF	BLYP	B3LYP	MP2	QCFF <sup>b</sup>
$r_1$	1.464	1.468	1.460	1.455	1.450
$r_2$	1.330	1.369	1.355	1.363	1.360
$r_3$	1.478	1.482	1.475	1.467	1.471
$r_4$	1.333	1.369	1.356	1.362	1.377
$r_5$	1.503	1.504	1.491	1.490	1.496

<sup>a</sup> Full sets of Cartesian coordinates for all geometries are available in the Supporting Information. <sup>b</sup> Semiempirical CI-method,<sup>24</sup> taken from ref 5.

More interestingly, the spectra obtained during the stepwise photocleavage of the pentalene dimer show the presence of an intermediate which reveals itself mainly by a pair of sharp peaks at 299 and 311 nm. Clearer insight into the formation and decay of this intermediate can be obtained by alternating photolyses at 254 (formation) and 313 nm (bleaching) as documented by the series of difference spectra in Figure 2: After 15 min of irradiation at 254 nm we observe (apart from the decrease of the dimer precursor bands) in addition to an increase of the broad pentalene band a sharper increase of the above-mentioned pair of intermediate bands (trace 1). Short subsequent irradiation at 313 nm (which does not affect the pentalene dimer) leads to a bleaching of those bands accompanied by a further increase of the pentalene band, notably also that at 260 nm (trace 2). The same cycle can be repeated although the second time the formation and decay of the intermediate is less pronounced (spectra 3 and 4).

Concomitant IR measurements revealed a number of IR bands which grow and decay in concert with the 299/311-nm peaks in the UV spectrum, but these were mostly in a region ( $600\text{--}1000\text{ cm}^{-1}$ ) where not much structural insight can be obtained. Thus we are forced to speculate about the nature of this intermediate, but the only reasonable hypothesis which we can conceive involves stepwise cleavage of the bonds in the four-membered ring of the pentalene dimer **2** to yield first a bis-(vinylcyclopentadienyl) biradical **7** which decays to two molecules of pentalene **1**. Based on this hypothesis we attempted to record an ESR spectrum of this biradical, but this venture proved unsuccessful, presumably because the through space and/or through bond coupling between the two vinylcyclopentadienyl units is sufficiently strong to stabilize the singlet over the triplet state.

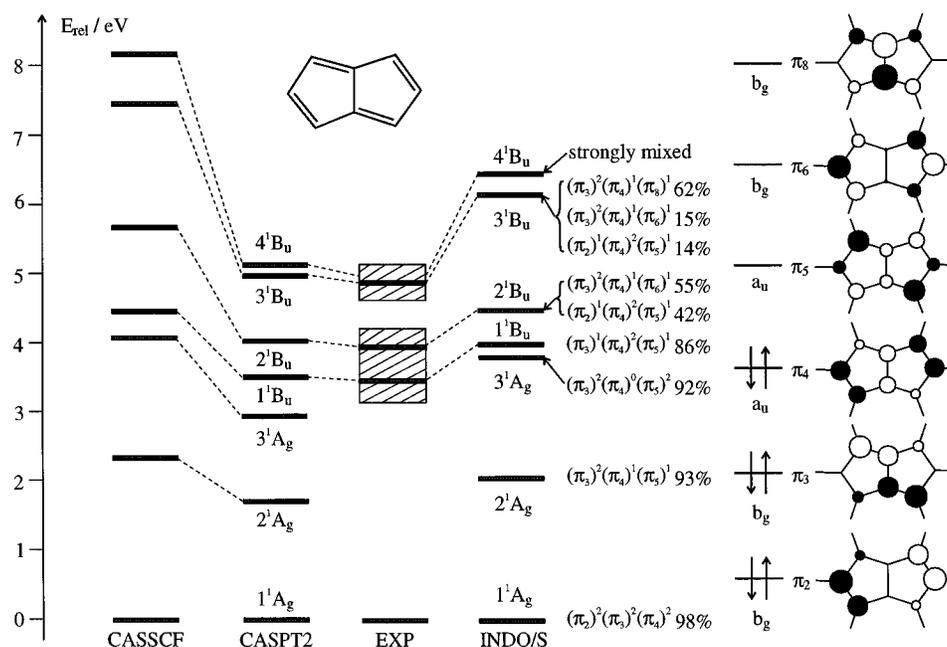
Finally we should mention that we attempted to re-form the dimers by warming the matrices to their annealing temperature of  $\approx 30$  K, but we could see no dimerization under these conditions. However, when the same reaction was carried out in a frozen Freon glass ( $\text{CF}_3\text{Cl}/\text{CF}_2\text{BrCF}_2\text{Br}$ ), the EA spectrum of the dimer was re-formed on slight warming (which leads to thawing of this particular glass).

**2. Molecular and Electronic Structure.** Table 1 shows the geometries of pentalene as obtained by different methods of ab initio theory within  $C_{2h}$  symmetry which corresponds to that of the ground state equilibrium structure.<sup>7,8,22</sup> From this we note that the pronounced C–C bond length alternation found

**Table 2.** Calculated and Observed Excited State Energies of Pentalene

	QCFF-CI <sup>a</sup>		INDO/S (CIS) <sup>b</sup>		INDO/S (CISD) <sup>c</sup>		CASSCF <sup>d</sup>		CASPT2		exp <sup>e</sup> ΔE/eV
	ΔE/eV	<i>f</i>	ΔE/eV	<i>f</i>	ΔE/eV	<i>f</i>	ΔE/eV	<i>f</i>	ΔE/eV	<i>f</i>	
1 <sup>1</sup> A <sub>g</sub>	(0)		(0)		(0)		(0)		(0)		(0)
2 <sup>1</sup> A <sub>g</sub>	1.48	0	1.98	0	2.02	0	2.39	0	1.69	0	
3 <sup>1</sup> A <sub>g</sub>					3.87	0	4.17	0	2.91	0	
4 <sup>1</sup> A <sub>g</sub>	6.05	0	5.85	0	5.71	0					
1 <sup>1</sup> B <sub>u</sub>	3.52	0.27	3.77	0.164	4.00	0.153	4.47	0.016	3.50	0.012	3.48 <sup>g</sup>
2 <sup>1</sup> B <sub>u</sub>	4.47	0.18	5.12	0.110	5.23	0.084	5.69	0.062	3.99	0.044	3.94 <sup>g</sup>
3 <sup>1</sup> B <sub>u</sub>	6.07	1.26	5.87	0.287	6.26	0.314	7.51	0.210	5.01	0.140	4.80 <sup>g</sup>
4 <sup>1</sup> B <sub>u</sub>			6.14	1.003	6.44	0.966	8.27	0.086	5.06	0.053	(4.85) <sup>h</sup>
1 <sup>1</sup> A <sub>u</sub>			5.42	0.001			6.95	≈0	4.92	≈0	
2 <sup>1</sup> A <sub>u</sub>			5.56	0.002			8.88	≈0	6.61	≈0	
1 <sup>1</sup> B <sub>g</sub>			5.62	0			8.87	0	4.95	0	
2 <sup>1</sup> B <sub>g</sub>			6.08	0			10.49	0	6.52	0	

<sup>a</sup> Semiempirical Method.<sup>5</sup> <sup>b</sup> Only single excitations. <sup>c</sup> Including the HOMO → LUMO doubly excited configuration. <sup>d</sup> See text for definition of active space. <sup>e</sup> Present work. <sup>f</sup> "Doubly excited" state. <sup>g</sup> Maxima of deconvoluted bands, see Figure 1. <sup>h</sup> Band maximum not discernible, assumed to be shifted to slightly higher energy than that of 3<sup>1</sup>B<sub>u</sub>.



**Figure 3.** Electronic structure of pentalene by experiment and calculation. The shaded areas in the column labeled EXP indicate the widths of the observed bands at 30% height, and the solid bars correspond to the maxima of the Gaussians used in the deconvolution. The INDO/S column shows the results obtained with inclusion of the HOMO → LUMO doubly excited configuration. Configurations are indicated in terms of the MO's shown on the right. The symmetry is  $C_{2h}$  and all numbers are listed in Table 2.

at the HF level ( $\Delta r = 14.5\text{--}17.7$  pm around the periphery) is attenuated by dynamic correlation (to  $\Delta r = 10\text{--}13.5$  pm). As usual, all bond lengths are shorter by  $\approx 1$  pm in B3LYP than in BLYP due to the admixture of HF density in the latter method, but apart from that the geometries are very similar by all correlated methods. Due to our good recent experience with BLYP in a project on  $C_7H_6$  hydrocarbons<sup>23</sup> we decided to employ these geometries in the subsequent electronic structure calculations, but the B3LYP or MP2 geometries would surely have served as a similarly good basis.

In an effort to model the EA spectrum of pentalene and to understand its excited state electronic structure, we performed

(22) We have also carried out calculations under enforced  $D_{2h}$  symmetry in an attempt to calculate the activation barrier for the automerization process in pentalene. Thereby we found, however, that the reaction probably does not proceed on a closed shell singlet surface throughout (cf. ref 8). We will clarify this matter in a separate publication on the electronic structure of  $D_{2h}$  pentalene (Bally, T.; Zhu, Z. To be submitted for publication).

(23) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535.

CASSCF/CASPT2 and INDO/S calculations at the BLYP geometry. The corresponding results are listed in Table 2 and displayed graphically in Figure 3. If we focus first on the electric dipole allowed  $1^1A_g \rightarrow 1^1B_u$   $\pi \rightarrow \pi^*$  transitions we note that CASPT2 gives excellent agreement with experiment, if we assume that the asymmetric broad near-UV band of pentalene comprises *two* electronic transitions at 356 and 315 nm. Indeed, the shape of this absorption band can be modeled quite well with two Gaussian curves centered at these wavelengths (cf. top part of Figure 1). In the region of the 260-nm band CASPT2 also predicts two excited states which could jointly contribute, both at slightly higher energy, but within the error bounds of this procedure. Thus we propose that this band contains also two transitions, one being perhaps much weaker than the other such that it does not show up prominently. Unfortunately, intruder states in the CASPT2 calculations prevented us from calculating the position of the intense band which rises below 230 nm. It must correspond to the next higher  $1^1B_u$  state, and INDO/S indeed predicts several  $1^1A_g \rightarrow 1^1B_u$  transitions with high oscillator strengths at higher energies. From the same calcula-

tions we gather that the  $1^1B_u$  state is predominantly  $\pi_2 \rightarrow \pi_4$  excited, the higher ones comprise several excited configurations.

Turning to the  $A_g$  states which we do not observe in our experiments, we noted to our surprise that *two* of them lie below the lowest  $1^1B_u$  state. Analysis of the CASSCF wave function revealed why the second of them (around 425 nm) was missed by all previous calculations: it is dominated by the HOMO  $\rightarrow$  LUMO doubly excited configuration which also contributes significantly to the  $2^1A_g$  state and to the ground state but which is ignored in the usual semiempirical CI calculations such as INDO/S<sup>19</sup> or QCFF-PI.<sup>24</sup> When this configuration is included in the INDO/S calculation it also shows up prominently in the second excited state (cf. Figure 3) and its admixture to the ground state caused the gap to the  $1^1B_u$  excited states to increase significantly. Of course INDO/S (as most other semiempirical electronic structure methods) was not parametrized to account for doubly excited configurations, so quantitative accuracy cannot be expected from calculations including such states. However, the example of pentalene should remind us that one should nevertheless remain watchful of such states.

Of course, this prominent role of a doubly excited configuration should have come as no surprise in view of the  $\pi$  orbital structure of pentalene: contrary to the case of linear conjugated polyenes where the HOMO  $\rightarrow$  LUMO doubly excited configuration (which also plays a very important role in the polyene's electronic structure and photophysics)<sup>25</sup> mixes with singly excited configurations which arise from HOMO-1  $\rightarrow$  LUMO and from HOMO  $\rightarrow$  LUMO+1 excitation, in pentalene the HOMO  $\rightarrow$  LUMO singly and doubly excited configurations happen to be of the same symmetry and are therefore predisposed for efficient mixing. In addition it turns out that due to differences in electron repulsion the doubly excited configuration lies at much less than twice the energy of the singly excited one (3.6 vs 2.1 eV in INDO/S) such that it is the second excited one already at the one-electron configuration level.

We also calculated the lowest two excited states of  $A_u$  and  $B_g$  symmetry, respectively, which involve excitations from  $\sigma$  or into  $\sigma^*$  MO's (see last four rows of Table 2). Although the first of these coincides approximately with the  $3^1B_u$  and  $4^1B_u$  states, the oscillator strengths are minute or zero, so that no spectroscopic manifestation of these states is to be expected. Furthermore, it is to be expected that Rydberg states, which we have excluded from consideration, will contribute strongly in the far-UV region which we did not probe in our experiments.

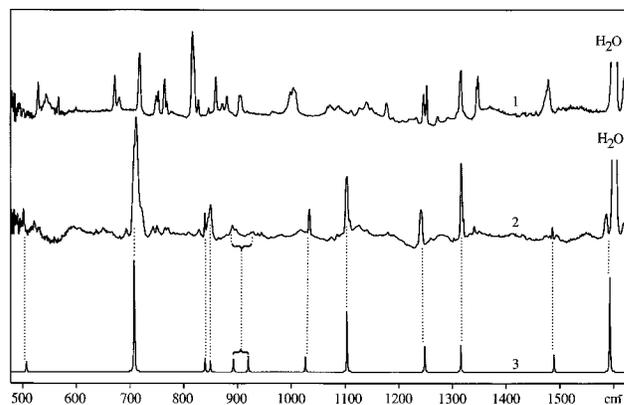
Finally we would like to comment on the interpretation of the EA spectrum of 1,3,5-tri-*tert*-butylpentalene in the light of the present findings: There, two clearly resolved bands are seen in the near-UV with maxima at about 340 and 280 nm (3.65 and 4.42 eV) which were attributed to the  $S_0 \rightarrow S_2$  and  $S_0 \rightarrow S_3$  transitions.<sup>4d,5</sup> On the other hand, the band at 257 nm in pentalene (and  $\approx 270$  nm in 1,3-dimethylpentalene<sup>4b</sup>) appears to be missing in the spectrum of the 1,3,5-tri-*tert*-butyl derivative which shows, however, the intense band at 215 nm which is also present (albeit not resolved) in the parent compound and in the methylpentalenes.

We have calculated the shifts of the different EA bands introduced by the three *tert*-butyl groups by INDO/S (see Table 3). Thereby we found that the position of the  $1^1B_u$  state is lowered by only 0.13 eV by alkylation whereas the  $2^1B_u$  state is stabilized by 0.45 eV, i.e. the first two  $2^1B_u$  states which are split by  $\approx 0.4$  eV in parent pentalene are expected to be nearly coincident in the *tert*-butyl derivative.<sup>26</sup> In qualitative accord

**Table 3.** Comparison of the INDO/S Predictions<sup>a</sup> of the Excited States of Pentalene and Its 1,3,5-Tri-*tert*-butyl Derivative

state	pentalene			1,3,5-tri- <i>tert</i> -butylpentalene			state
	$\Delta E/eV$	$f$	exp <sup>b</sup>	$\Delta E/eV$	$f$	exp <sup>c</sup>	
$1^1A_g$	(0)		(0)	(0)		(0)	$1^1A''$
$2^1A_g$	2.02	0		1.72	0.004	2.06	$2^1A''$
$3^1A_g$	3.87	0		3.40	0.006		$3^1A''$
$1^1B_u$	4.00	0.15	3.48	3.87	0.12	3.67	$4^1A''$
$2^1B_u$	5.23	0.08	3.94	4.78	0.05	3.67	$5^1A''$
$3^1B_u$	6.26	0.31	4.80	5.79	0.41	4.42	$6^1A''$
$4^1B_u$	6.44	0.96	4.80	6.02	0.89	4.42	$7^1A''$
$5^1B_u$	$e$		(>6.0) <sup>d</sup>		$e$	5.76	$8^1A''$

<sup>a</sup> CI including the HOMO  $\rightarrow$  LUMO doubly excited configuration (see text). <sup>b</sup> This work. <sup>c</sup> Ref 5. <sup>d</sup> Only onset of band seen. <sup>e</sup> INDO/S predicts many intense transitions at >7 eV.



**Figure 4.** IR spectra of the pentalene dimer before (1) and after complete photodecomposition (2). The bottom trace (3) represents the spectrum obtained from the BLYP force field scaled as indicated in the text.

with CASPT2, the next two  $1^1B_u$  states are also predicted by INDO/S to lie close in energy,<sup>26</sup> but  $\approx 0.4$  eV lower than in parent pentalene where we assign both to the band at 257 nm. Thus we expect a band comprising these two states around 280 nm, i.e. exactly where the band which had been assigned to the  $S_0 \rightarrow S_3$  transition in tri-*tert*-butylpentalene<sup>5</sup> occurs (INDO/S probably also overestimates the oscillator strengths for these transitions).

Based on the above we propose that the bands at 340 and 280 nm comprise, as in parent pentalene, *two* excited states each. If we additionally take into account the occurrence of the doubly excited state below the onset of the dipole allowed transitions, then the first strong EA band contains the  $S_0 \rightarrow S_3$  and  $S_0 \rightarrow S_4$  and the second one the  $S_0 \rightarrow S_5$  and the  $S_0 \rightarrow S_6$  transitions in all pentalene derivatives. We do not claim that our interpretation of the excited state structure of pentalene is definitive, but it is based on what must be considered state-of-the-art calculations (CASPT2) which have proven to give reliable predictions in many related cases.

**3. IR Spectrum and Vibrational Structure.** In Figure 4 we show the IR spectra of the precursor dimer (trace 1) in argon and the spectrum that results after its complete photodegradation (trace 2). A comparison with a spectrum calculated by BLYP/6-31G\* (scaled with one factor, see below) shows excellent agreement with the latter in that only a few of the weakest observed IR peaks cannot be attributed to fundamentals of

(26) Note that INDO/S overestimates the absolute energies of the transitions to the  $1^1B_u$  states by varying amounts if we take experiment and/or CASPT2 as a reference (as explained in the text, this is partially due to the inclusion of the lowest double excited configuration which depresses the ground state). However, we believe that the shifts introduced by the alkyl groups should still be modeled qualitatively correctly.

(24) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5612.

(25) See, e.g.: Hudson, B. S.; Kohler, B. E.; Schulten, K. *Excited States* **1982**, *6*, 1.

**Table 4.** Calculated and Observed IR-Active Fundamentals of Pentalene<sup>24</sup>

	experimental		calculated <sup>a</sup>		PED <sup>c</sup>
	<i>E/cm</i> <sup>-1</sup>	int <sup>b</sup>	<i>E/cm</i> <sup>-1</sup>	int <sup>b</sup>	
A <sub>u</sub>	892	8	892.9	11	60.7% w, 39.3% p
	852	15	850.2	10	80.0% w, 20.0% p
	712	100	707.9	100	95.8% w, 4.2% p
	502	2	507.5	9	33.3% w, 66.7% p
			297.9	1	5.7% w, 94.3% p
			166.3	5	3.8% w, 96.2% p
B <sub>u</sub>	1588	9	1594.2	55	82.5% s, 13.2% r, 4.0% d
	1488	1	1490.2	10	85.7% s, 10.8% r, 2.8% d
	1318	21	1316.2	16	18.1% s, 77.2% r, 4.6% d
	1242	16	1249.0	14	12.8% s, 79.0% r, 8.1% d
	1104	23	1104.3	37	36.1% s, 60.5% r, 3.4% d
	1034	3	1027.6	9	50.3% s, 33.3% r, 16.2% d
	927	2	921.9	9	66.0% s, 20.2% r, 13.8% d
	840	3	840.8	9	2.5% s, 3.3% r, 94.1% d
			438.4	3	37.5% s, 4.2% r, 58.3% d

<sup>a</sup> From scaled BLYP force field as described in text. <sup>b</sup> Intensity relative to base peak at 712 cm<sup>-1</sup>. <sup>c</sup> Percent potential energy distribution (w, C–H wag, p, ring puckering, s, C–C stretch; r, C–H rock, d, planar ring deformation).

pentalene. We are aware that a single IR spectrum constitutes no structural proof, but it would be difficult to imagine how such good agreement between calculation and experiment could be fortuitous. Conceptually, the synthetic pathways to the pentalene dimer<sup>11</sup> can be readily adapted to the perdeuterio species which would indeed be very useful for a further clarification of the vibrational structure. Also, IR and Raman spectra are completely complementary (and mutually exclusive) for molecules of *C*<sub>2h</sub> symmetry, so the Raman spectra of pentalene would also constitute a valuable extension of our present work.

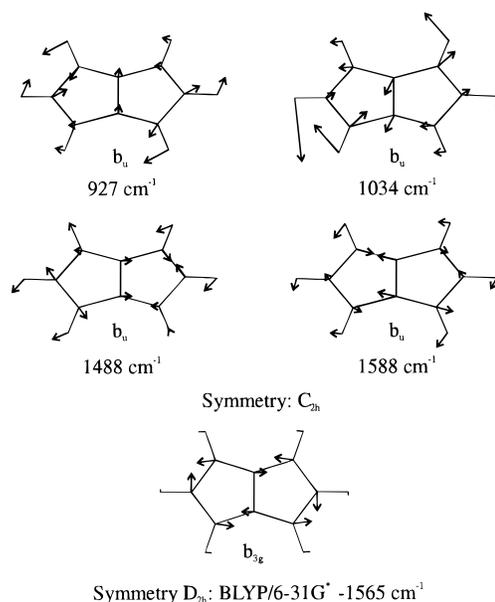
Meanwhile we will rationalize the vibrational structure of pentalene on the basis of the presently available data and the BLYP calculations which model them so well. In *C*<sub>2h</sub> symmetry, the 36 internal degrees of freedom of pentalene are shared by 18 IR-active (13 in-plane b<sub>u</sub> and 6 out-of-plane a<sub>u</sub>) and 18 Raman-active (13 in-plane a<sub>g</sub> and 5 out-of-plane b<sub>g</sub>) normal modes. If we exclude those and the three b<sub>u</sub> C–H stretches which we did not monitor, there are 15 IR-active fundamentals, three of which we did not observe because their frequencies are predicted to lie below the current range of our apparatus.

In order to analyze the modes responsible for the observed IR bands, we transformed the BLYP Hessian into a set of internal coordinates defined according to the standards proposed by Pulay et al.<sup>27</sup> In accord with recent findings of Rauhut and Pulay<sup>28</sup> we usually find it necessary to slightly scale up the BLYP force constants for out-of-plane modes and ring deformations to achieve optimal agreement with experiment. Due to the scarcity of experimental data, we limited ourselves to a single scaling factor of 1.04 for these two types of modes, leaving all others unscaled, which resulted in a root-mean-square deviation between the 12 observed and calculated fundamentals of only 4.2 cm<sup>-1</sup> (cf. Table 4).<sup>29</sup> Thus we have a degree of confidence that the force field which reproduces the experimental data so well is a reasonable basis for normal mode and force constant analyses.

(27) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *31*, 181.

(28) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(29) The list of all calculated fundamentals, along with those for the perdeuterated derivative, is given in the supplementary material for future reference. They appear in the form of the output of our normal mode analysis program<sup>15</sup> which also lists the internal coordinate definitions, the potential energy distributions, and the force constant matrices in internal and in symmetry coordinates.



**Figure 5.** Representation of the normal modes for the four b<sub>u</sub> fundamentals which involve strong contributions of C–C stretches (note that each of them involves predominantly the deformation of only one pair of symmetry equivalent bonds, cf. text and Table 3).

These show that the most intense band in the IR spectrum of pentalene (712 cm<sup>-1</sup>) is due to a combination of C–H wags whereas the modes giving rise to the three prominent bands between 1100 and 1320 cm<sup>-1</sup> are dominated by contributions from C–H rocking deformations (60–75% in potential energy). It is the weaker features at 1588, 1488, 1034, and 927 cm<sup>-1</sup> that are associated predominantly with C–C stretching modes—obviously the most interesting ones—which are depicted in Figure 5. An analysis of these shows that the deformations of the symmetry equivalent single and double bonds are quite well separated in different normal modes: 56.2% of the potential energy contribution to the 1588-cm<sup>-1</sup> mode is from the bridgehead double bond stretches and 62.2% of that to the 1488-cm<sup>-1</sup> mode is from the other double bond stretches (with less than half as much from other stretches). The 927-cm<sup>-1</sup> vibration is ascribed to 63.5% by the outer single bond stretches whereas those of the single bonds emanating from the bridgehead are spread between the 1034- and the (unobserved) 438-cm<sup>-1</sup> vibration.

A consequence of the above is that there is no single normal mode which can be associated with the reaction coordinate for automerization of pentalene via a *D*<sub>2h</sub> structure, i.e. which annihilates the strong bond length alternation which prevails in the *C*<sub>2h</sub> equilibrium structure. Therefore substantial mode mixing must take place during the automerization process if this occurs via a *D*<sub>2h</sub> transition state.<sup>22</sup>

As a final comment we note that an analysis of the *excited state* vibrational structure of pentalene would constitute a very interesting endeavor in view of the recent work where such an analysis revealed that the  $\pi$ -electrons in *aromatic* systems are distortive and that the observed lack of bond alternation in such systems must therefore be due to restoring forces of the  $\sigma$  frame.<sup>30</sup> This effect is more pronounced in antiaromatic molecules such as cyclobutadiene, or the present case of pentalene, where the  $\pi$ -distortive effects win against the symmetry-restoring  $\sigma$ -forces to create structures with strongly alternating single and double bonds.

However, HOMO  $\rightarrow$  LUMO excitation should lead to a mitigation of  $\pi$  electron's distortive power (especially if two

(30) Shaik, S.; Zilberg, S.; Haas, Y. *Acc. Chem. Res.* **1996**, *29*, 211.

electrons are excited, as in the  $S_0 \rightarrow S_2$  transition, cf. Section 2.2 above) and to a corresponding attenuation of the bond length alternation, as in cyclobutadiene<sup>31</sup> where the first excited state in  $D_{2h}$  has a  $D_{4h}$  minimum. Indeed, the recent QCFF-PI calculations showed that the equilibrium structure of the  $S_1$  state has  $D_{2h}$  symmetry, i.e. pentalene appears to be another anti-aromatic molecule where the  $\pi$ -distortive force is attenuated on electronic excitation to the extent that bond alternation disappears.<sup>31</sup> Unfortunately, we did not observe the first two excited states (which are the ones that involve HOMO  $\rightarrow$  LUMO excitation, cf. above), but perhaps future experiments may be used to probe this.

#### 4. Conclusion

Photocleavage of the *syn-cis* dimer of pentalene in Ar/N<sub>2</sub> matrices proceeds stepwise, presumably via a bis(vinylcyclopentadienyl) biradical. The overall decomposition leads to clean samples of parent pentalene which has been observed for the first time by electronic absorption and infrared spectroscopy.<sup>32</sup> Modeling of the electronic structure by the CASPT2 and INDO/S methods reveals that the observed near-UV band of pentalene (and its alkylated derivatives) contains *two*  $^1A_g \rightarrow ^1B_u$  transitions, but that *two*  $^1A_g$  excited states lie below this energy, one of them being predominantly of doubly excited nature. These findings suggest a re-interpretation of the previous electronic spectra of pentalene derivatives.<sup>4–6</sup>

Twelve out of the eighteen  $a_u$  and  $b_u$  fundamentals of

(31) In cyclobutadiene, the first excited (singlet or triplet) state in  $D_{2h}$  has its minimum at  $D_{4h}$  symmetry (see, for example: Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343).

(32) We have made various attempts to record NMR spectra of pentalene, but its high reactivity precluded any productive measurements. Presumably, photolysis in the solid state combined with the CP-MAS technique could provide chemical shifts and thus a basis for discussion of ring-current effect.

pentalene were observed and assigned in the IR spectrum. After scaling the force constants for out-of-plane and ring-deformation modes with a single factor of 1.04, a BLYP/6-31G\* force field reproduces the observed vibrational frequencies with a root-mean-square deviation of 4.2 cm<sup>-1</sup>. A normal mode analysis based on this force field shows that—in contrast to other conjugated hydrocarbons—there is no single mode associated with a decrease of bond alternation because the stretches of the different symmetry-equivalent single and double bonds contribute to separate fundamentals. Consequently, substantial mode mixing is required on the way to the  $D_{2h}$  transition state for automerization of pentalene.

Finally, we propose that upon HOMO  $\rightarrow$  LUMO excitation, the strongly distortive force of the  $\pi$ -electrons may be alleviated to the point where the structure of pentalene becomes symmetric, in contrast to aromatic systems where the distortive power of the  $\pi$ -electrons is weaker and where electronic excitation leads only to a lowering of the frequency for the so-called Kekulé mode which enhances bond alternation.<sup>30</sup> Previous semiempirical calculations<sup>5</sup> seem to support this notion which could be probed by studying the excited state vibrational structure of pentalene

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**Supporting Information Available:** Sets of full Cartesian coordinates for all structures of **1** listed in Table 1 and full results of normal mode analysis for **1** and **1-d<sub>6</sub>** (14 pages). See any current masthead page for ordering and Internet access instructions.

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