Molecular Orbital and Strain Energy Investigations of the Photocyclization of 1,2-Di-β-naphthylethylene

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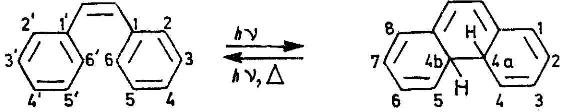
The formation of 4a,4b-dihydrophenanthrene (II), 10b,10c-dihydrodibenzo[*c,g*]phenanthrene (IV), and 14a,14b-dihydrodibenzo[*b,g*]phenanthrene (V) and their ground and excited state processes are correlated by MO and strain energy minimalization analyses.

IN a previous study,[1] we reported on the MO analysis of the excited and ground state reactivity in system (A) [*cis*-stilbene (I) $\rightleftarrows$ 4a,4b-dihydrophenanthrene (II) (DHP)]. In this paper we extend this investigation to system (B).† Aspects of the photochemistry of this system have been treated at length by Wismonski-Knittel *et al.*[2a]



(I) (II) (A)

Our aim is to determine by MO and strain energy analyses the factors responsible for features (a)—(e) particular to system B. (a) The photocyclization of (III) gives (IV) and the unstable isomer (V) but none of

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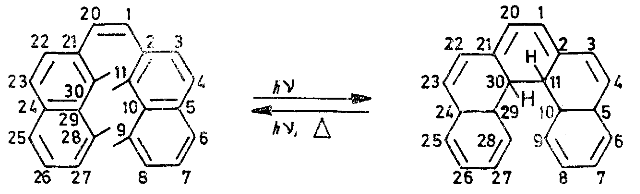
† The numbering of atoms shown in formulae (I), (III), and (IV) is adopted for reasons of convenience. The three conformers of (III) are denoted (IIIa—c).

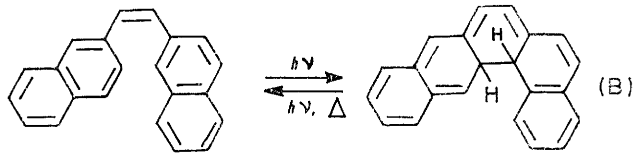
[1] K. A. Muszkat and W. Schmidt, *Helv. Chim. Acta*, 1971, **54**, 1195.

[2] (*a*) T. Knittel-Wismonski, G. Fischer, and E. Fischer, *J.C.S. Perkin II*, 1974, 1930; (*b*) M. Scholz, M. Muhlstadt, and F. Fietz, *Tetrahedron Letters*, 1967, 665; (*c*) Ch. Goedicke and H. Stegemeyer, *Ber. Bunsengesellschaft. Phys. Chem.*, 1967, **73**, 782.

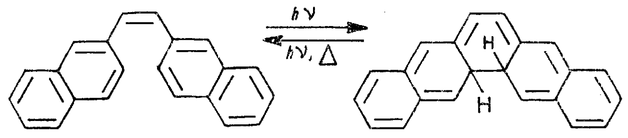
(VI).[2,3] (b) The photocyclization process in (A) and in its ring-substituted derivatives has a low (12 kJ mol^{-1}) potential barrier.[4,5] In (B), the photocyclization (III) $\longrightarrow$ (IV) is strongly temperature dependent, due to an energy barrier of *ca.* 42 kJ mol^{-1} [2a,3,6] The path (III) $\xrightarrow{h\nu}$ (V) is much less temperature dependent.[2a,3] (c) The photochemical ring opening process of (II) has a high (*ca.* 0.70) and temperature independent quantum yield (measured down to 90 K).[4] At 25° this process, (IV) $\xrightarrow{h\nu}$ (III), is 100 times less efficient than in (A) and is markedly temperature dependent (activation energy of *ca.* 27.3 kJ mol^{-1}).[2a,3,6] (d) The thermal ring opening reaction [DHP $\xrightarrow{\Delta}$ (I)] for DHP and for many of its derivatives is fast at ambient temperatures.[4] The same process in (IV) is slower than in DHP by a factor of 150. The thermal stability of (V) is however lower than that of (IV) by a factor of *ca.* 10^{10}.[2a,3] The activation energies for the ring opening process are (II), 73.5;[4] (IV), 113; and (V), 50 kJ mol^{-1}. (e) DHP and its derivatives are nonfluorescent[3] due to the very efficient ring opening process in the first excited singlet state. On the other hand, (IV) is strongly fluorescent, the limiting low temperature fluorescence quantum yield being 0.70.[6]



(IIIa) (IV)



(IIIb) (V)



(IIIc) (VI)

In the following discussion we shall assume that *cis*-di-β-naphthylethylene (III) exists in three distinct conformations (IIIa—c).

Molecular Geometries.—The first step consists in calculating the molecular geometry of the reactant and product molecules by a strain energy minimalization technique.[7] This step is required because no experimental geometry data are available for these molecules. In its main features our strain energy minimalization computer program is based on the principles outlined by Wiberg.[8] Whenever possible, full use is made of the molecular symmetry. Initial trial geometries were obtained from Dreiding models, or inferred from available data on similar molecules. Initial bond length values assumed were C–C 1.54; C=C 1.34; C=C(benzene) 1.40; C–C(next to double bond) 1.46; C–H(aliphatic) 1.1; and C–H(aromatic) 1.08 Å. The parameters and functions for the nonbonded interactions were taken from Williams[9a] (set III), and those for bond torsions from Kitaigorodsky and Dashevsky.[9b] All nonbonded interactions (excluding 1,3 interactions) were considered. Bond angle (θ) bending energy, E_θ, and torsional energy through angle ϕ, E_ϕ, are estimated from equations (1) and (2) where A and B are the respective double and

$$E_\theta = 0.0259(\theta - \theta_0)^2 \qquad (1)$$

$$E_\phi = 64A \sin^2 \phi + 2.5B(1 - \cos 2\phi) \qquad (2)$$

single bond characters calculated from the bond lengths.[7,9b] The minimalization was carried out by the steepest descent method. All the conformers of (III), as well as (I), are strongly twisted in the ground state about the single central bonds and weakly twisted about the central double bond. Thus, in (IIIa), $\phi(20,1,2,3) = 32$, $\phi(21,20,1,2) = 8°$; in (I) $\phi(7',7,1,2) = 31$, $\phi(1',7',7,1) = 8.5°$. The molecules (IV)—(VI) as well as (II) are all heavily twisted, this deformation being required because of strong nonbonded interactions (see below). The largest deformation is the torsion about the C(4a)–C(4b) bond *e.g.* in (IV) $\phi(10,11,30,29) = 95°$, while in (II) $\phi(4,4a,4b,5) = 64°$. Other strong deformations in (IV) are $\phi(11,2,3,4) = 23$, $\phi(5,10,11,2) = 28$, and $\phi(10,11,2,3) = 27°$. The corresponding deformations in (II) are much smaller. The optimized geometries of (I), (II), (IIIa), (IIIc), (IV), and (VI) have C_2 symmetry. [Accordingly only one value for symmetry related internal co-ordinates is reported.] The short distances in (IIIa) and in (IV) are listed in Table 1.

TABLE 1

Short distances (Å) in (III) and in (IV) with corresponding values for (I) and (II) in parentheses

	Atoms	Distance	Atoms	Distance
(IIIa)	11–30	2.87 (2.8)	H(11)–H(30)	2.98 (3.0)
(IV)	H(30)–H(9)	1.95	H(9)–H(28)	2.16
	9–28	2.95		
(II)	H(4a)–H(5)	2.5		

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[3] T. Wismonski-Knittel, T. Bercovici, and E. Fischer (*a*) *J.C.S. Chem. Comm.*, 1974, 716; (*b*) personal communication.

[4] K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662.

[5] A. Bromberg, K. A. Muszkat, and E. Fischer, *Israel J. Chem.*, 1972, **10**, 765.

[6] T. Knittel, G. Fischer, and E. Fischer, *J.C.S. Chem. Comm.*, 1972, 85.

[7] R. Korenstein, K. A. Muszkat, and S. Sharafi-Ozeri, *J. Amer. Chem. Soc.*, 1973, **95**, 6177.

[8] K. B. Wiberg, *J. Amer. Chem. Soc.*, 1965, **87**, 1070.

[9] (*a*) D. E. Williams, *J. Chem. Phys.*, 1966, **45**, 3770; (*b*) A. I. Kitaigorodsky and V. G. Dashevsky, *Tetrahedron*, 1968, **24**, 5917.

The value obtained by the present method for the 11—30 bond of (IV) is 1.565 Å. In (II) this bond length is 1.54 Å.

Energetics of System (*B*).—Systems (A) and (B) were analysed using the MINDO/2[10] and the Extended Hückel[11] (EH) methods and parametrizations. The calculated ground state energies are: (IV) relative to (IIIa) +210 (MINDO/2), +227 kJ mol^{-1} (EH), (II) relative to (I), +108 (MINDO/2), +122 kJ mol^{-1} (EH). The comparison with thermochemical data is given in the Appendix.

The experimental first singlet excitation energies amount to (approximate values for 0,0 transitions): (IIIa), 328; (IV), 248 kJ mol^{-1}, while the values calculated by the P–P–P method[12] (vertical transitions) are respectively 357 and 273 kJ mol^{-1}. One conclusion that may be drawn from these data is that in this photocyclization (IV) is formed in its electronic ground state. While this conclusion might also be true for other DHP derivatives it necessarily holds in the case of system (B). According to the EH results, (V) is less stable than (IV) by 18 kJ mol^{-1}.

Part of the destabilization of the ground state configuration of (IV) relative to that of (IIIa) is due to purely steric factors (*i.e.*, displacement of internal co-ordinates from their minimum energy values and close approach of nonbonded atoms). Our strain energy calculation[7] indicates that the strain energy of (IV) is higher by 109 kJ mol^{-1} than that of (IIIa). This value should be considered presently only as an estimate because the parameters used in our calculation were not optimized with respect to the strain energy. For comparison we find that the strain energies of (I) and of (II) in system (A) are approximately equal.

Excited State Reactivity of Compound (III).—Direct experimental evidence[13,14] has recently been obtained which shows that the photocyclization of stilbenes is a *conrotatory* electrocyclic[15] process. This fundamental result predicted previously from theoretical and from indirect experimental considerations,[1,4] has several important implications for the symmetric cases. (1) The reactant [(I) or (IIIa)] should possess C_2 symmetry. This requirement is in fact met by the minimum strain energy geometry. (2) Together with the data of ref. 4, this result definitely establishes that the photocyclization takes place in the first excited singlet state. (3) The 4a- and 4b-hydrogens [in (II)] or their counterparts in the other DHP molecules have *trans*-geometry as required by the C_2 symmetry.

The point to be considered first is the reactivity of (III). As mentioned previously the photocyclization of (III) involves at least one α-position resulting in (IV) and (V), the third possible path forming (VI), being excluded.[2a]

We have shown recently[16,*] that electronic overlap population analysis[17] is particularly useful for studying the reactivity of *cis*-stilbenes and of their analogues in the electrocyclic photocyclization reaction. The change in the electronic overlap population between centres k and l, on excitation of one electron from the topmost occupied MO to the lowest unoccupied MO, Δn(k,l), calculated for the ground state geometry of the reactants (*i.e.*, *cis*-stilbenes), is a measure of the excited state reactivity of atoms k and l. For $2p$ electrons the magnitude of Ω, the interaction (in eV) between the centres forming the new bond, is estimated as 10 Δn(k,l). Positive values of Ω (0.1—0.2 eV) indicate a bonding interaction which leads to the formation of a new bond between k and l. Negative or small positive values indicate antibonding or nonbonding interactions respectively, which do not lead to cyclization. In the case of azastilbenes, the relative amounts of the photocyclization isomers formed were found to correlate quite well with the calculated Δn(k,l) values.[16a]

The particular reactivity of (III) to give (IV) and (V) and no (VI), has been previously analysed using the sum of the excited state HMO free valences of the reacting atoms as the reactivity index.[2b,18] In the present study we have re-examined this problem using the overlap population method which has the following advantages over the other methods. (a) The interaction between k and l stems to a large extent from the non-planarity of (IIIa—c), *i.e.*, the overlap between the three pairs of $2p$ AOs centred on k and l is correctly accounted for only by an all valence electron method. (b) The electronic overlap population has a clear and straightforward physical meaning as a measure of electronic overlap interaction energy,[17] and these interactions are the direct sources of reactivity in the present systems.

Examination of the highest occupied and the lowest unoccupied EH MOs of (IIIa—c) leads to the following conclusions.[†] The 11—30 $2p_x$, $2p_y$, and $2p_z$ interactions in (IIIa) are antibonding in the highest occupied MO but bonding in the lowest unoccupied MO. The main contribution to the reactivity stems from the $2p_z$ interactions. In particular one should note that the signs of the $2p_z$ 11—30 interactions (see below) are determined

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[*] The value of Δn(k, l) of −0.012 reported for photocyclization path 10 (Table 2) in ref. 16*a* is in error. The correct value is Δn(k, l) = 0.0088. A second (unstable) intermediate has been recently observed in the photocyclization of α,β-dinaphthylethylene which is believed to result from photocyclization through this path (E. Fischer, personal communication).

[†] The origin of the axes is the midpoint of the 1—20 bond. The x-axis is along this bond; the y-axis lies in the H(1)C(1)C(20)-H(20) plane; the z-axis is perpendicular to this plane.

[10] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 590.

[11] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

[12] For the original references see A. Bromberg and K. A. Muszkat, *Tetrahedron*, 1972, **28**, 1265.

[13] Th. J. H. M. Cuppen and W. H. Laarhoven, *J. Amer. Chem. Soc.*, 1972, **94**, 5914.

[14] Ch. Goedicke and H. Stegemeyer, *Chem. Phys. Letters*, 1972, **17**, 492.

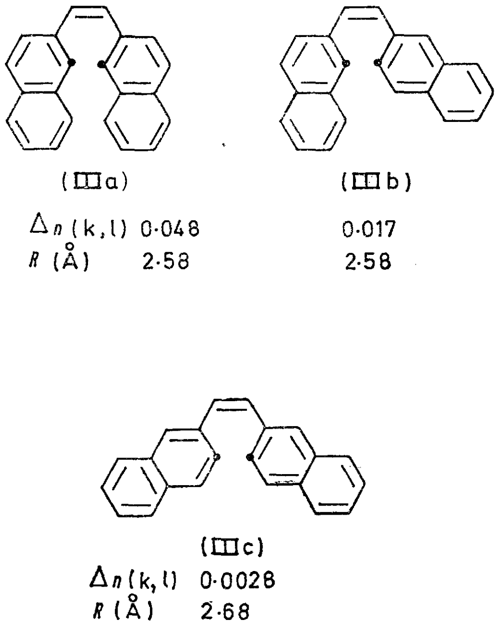
[15] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970.

[16] (*a*) K. A. Muszkat and S. Sharafi-Ozeri, *Chem. Phys. Letters*, 1973, **20**, 397; (*b*) K. A. Muszkat, G. Segar, and S. Sharafi-Ozeri, *J.C.S. Faraday II*, in the press.

[17] R. S. Mulliken (*a*) *J. Chem. Phys.*, 1955, **23**, 1833, 1841; (*b*) *J. Phys. Chem.*, 1952, **56**, 295.

[18] W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Rec. Trav. chim.*, 1968, **87**, 687.

by the displacements of these atoms along the z axis. In (IIIb) the $2p_z$ 11—30 interaction is only weakly bonding in the lowest unoccupied MO while in (IIIc) all the interactions are practically nil. The Δn(k,l) values (calculated from EH wavefunctions) for the reacting positions of the three conformers of *cis*-1,2-di-β-naphthylethylene, indicated by filled circles (k and l), and the calculated ground state equilibrium distances R(k,l) are as shown in the Scheme. From the Δn(k,l) values it is obvious that the formation of (VI) is very unlikely, and that there is a strong tendency to form (IV). The formation of (V) is an intermediate case.



SCHEME

The same trend of the Δn(k,l) values in (IIIa—c) is observed for slightly larger separations of the reacting centres, as may be inferred from the values in Table 2.

TABLE 2

	(IIIa)	(IIIb)	(IIIc)
Δn(k,l)	0.022	0.0022	0.0004
R(Å)	2.93	2.93	2.96

TABLE 3

Δn Values for nonreactive centres m, n of (IIIa and c) (R in Å)

	(IIIa)		(IIIc)	
m–n	Δn	R	Δn	R
2–21	0.0028	3.0	0.001	3.1
3–22	0	5.5	0	5.5
8–27	0.0002	4.6	0	7.0
9–28	0.0038	3.6	0	5.6
10–29	0	3.6	0.0034	3.6

These Δn(k,l) values for (IIIa) correspond to large bonding effects, *ca.* 0.5 at 2.58 and *ca.* 0.2 eV at 2.93 Å. Δn Values for other centres are listed in Table 3. Thus the Δn value for the atom pair forming the new bond is much larger than the Δn values for other atom pairs. The recent experimental reactivity data on the formation of (IV) and of (V) indicate that the ratio R = [(V)] : [(IV)] is strongly dependent on both temperature and wavelength of irradiation.[3] At room temperature R varies from 1.3 to 4.2 depending on the wavelength.[3] At lower temperatures [(IV)] drops sharply while [(V)] remains constant.[3] [(IV)] is highest at 330 K and then $\phi_{(V)} : \phi_{(IV)}$, the ratio of the cyclization quantum yields, is 0.82.

Considering the trend of the calculated Δn(k,l) values for (IIIa and b), the above results point to two possible conclusions. (1) Conformers (IIIa and b) [and possibly (IIIc)] exist as separate entities, each possessing a distinct absorption spectrum. (2) The concentrations of (IIIa and b) differ greatly, [(IIIb)] > [(IIIa)]; thus (IIIa) seems to be slightly less stable than (IIIb) [and (IIIc)]. Only at sufficiently high temperatures (*e.g.* >240 K) is (IIIa) present to any significant extent in the conformer mixture.*

Simple considerations of steric factors favour (IIIb and c) over (IIIa). We feel that a sufficiently reliable answer to this question is at present beyond the capabilities of either the current minimalization method or even of the more refined CFF–π electron method of Warshel and Karplus.[20,†]

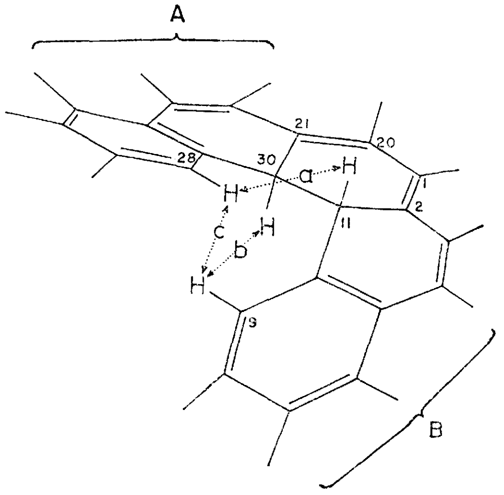


FIGURE 1 Ground state configuration of (IV)

Stability of the Ground and First Excited Singlet States of (IV) *and of* (V).—We attribute these differences between (II) and (IV) listed in the Introduction [points (c)—(e)] to the stabilizing effects, in the kinetic sense, of the steric repulsions on the electronic ground and excited states of (IV). From the data of Table 1 it is seen that in the ground state, (IV) has three strong interactions, *i.e.*, $a = b = 1.95$, $c = 2.16$ Å (*cf.* Figure 1). A qualitatively similar situation is expected to prevail in the

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* A recent X-ray structure determination indicates that in the crystal (III) assumes the (IIIb) conformation.[19]

† The ground state stability order calculated by the QCFF–PI method [20] is (IIIa) > (IIIc) > (IIIb).

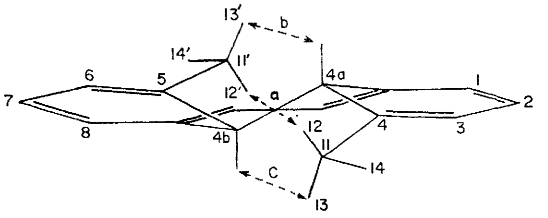
[19] D. Rabinovich and Z. Shakked, unpublished results.

[20] A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, 1972, **94**, 5612; A. Warshel and M. Levitt, program QCFF/P1 (QCPE program No. 247), Quantum Chemistry Program Exchange, Indiana University, Bloomington.

[21] L. S. Forster, *Theor. Chim. Acta*, 1966, **5**, 81.

first excited singlet state. Compared to (IV), (II) has only two, much milder steric interactions: H(4a)–H(5) = H(4b)–H(4) = 2.5 Å.

The most appropriate description of the reaction co-ordinate for the ring opening reaction of (IV) (either in the ground or in the excited state) seems to be a torsion of a naphthalene unit about the 1–2 or 20–21 bonds with a concomitant separation of centres 11 and 30 (*cf.* Figure 1).[1] Let us consider torsion of unit A about the bond 20–21. Clockwise torsion results in increased repulsion between H(9) and H(28). Counterclockwise torsion results in an increased H(9)–H(30) repulsion. These two repulsions hinder the ring opening process; an analogous result is obtained by considering the torsion of B about the 1–2 bond. Thus, with respect to the ring opening process, (IV) is contained in a potential well whose walls are provided by the H(9)–H(28) and H(9)–H(30) [or H(28)–H(11)] repulsions.

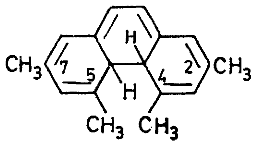


(VII)

FIGURE 2 Ground state configuration of (VII)

In (II), ring opening along an analogous reaction co-ordinate is not accompanied by any of these interactions, leading to a lower stability of the ground and first excited singlet states than in (IV), with the kinetic consequences mentioned earlier in points (c)—(e) in the Introduction.

Considerations similar to these are useful for understanding the pronounced lack of stability of the ground states of (V) [2a,3] and of 2,4,5,7-tetramethyl-4a,4b-dihydrophenanthrene (VII) (Figure 2). Both molecules revert thermally to the *cis*-stilbene even at —150°.[5]



(VII)

The difference in reactivity between (IV) and (V) with regard to ring opening, both in the ground and in the first excited states, also seems to be due to purely electronic factors. The importance of such factors may be judged from the electronic overlap population values, *n*(k,l), of the 11–30 bond in (IV) and its analogue in (V). These values indicate that in both states this bond is weaker in (V) than in (IV).

TABLE 4

EH electronic overlap populations of the 11–30 bond in (IV) and its analogue in (V)

	Ground state	First excited state
(IV)	0.7274	0.7086
(V)	0.7201	0.7008

Stability of the First Singlet Excited State of Compound (IIIa).—Compounds (I) and (IIIa) differ in the additional H(9)–H(28) interaction present in (IIIa). This interaction increases strongly as the 11–30 distance decreases during cyclization, resulting in an enhanced stability of the first singlet excited state of (IIIa) compared to the stability of this state in (I), with regard to photocyclization. The consequence of this increased stability of the first excited singlet state of (III) has been discussed in point (b) in the Introduction. The cyclization quantum yield is lowered [compared with that of (I)] and the cyclization process requires a rather large activation energy which, according to the present analysis, is required to counteract the steric repulsions [interactions a—c in (IV)] discussed in the previous section. For this same reason the photocyclization path to give (V) is much less temperature dependent.[2a]

Absorption Spectra of Compounds (IV) *and* (V).—The absorption spectra of (IV) [6] and of (V) [2a] are in several respects similar to those of the simpler 4a,4b-dihydrophenanthrenes.[3,21] The comparison between the observed and calculated (P–P–P method [12]) energies of the first two transitions and their intensity ratio is given in Table 5.

TABLE 5

	Observed		Calculated	
	E [a]	I_{rel} [b]	E	I_{re}
(IV)	2.74	2.1	2.84	2.6
	3.96		4.34 [c]	
(V)	2.15	2.1	2.25	2.4
	3.23		3.62 [c]	

[a] Transition energies in eV. [b] Relative intensity of second to first transition. [c] This is the third transition, the second being forbidden.

The agreement between calculated and observed excitation energies and relative intensities is satisfactory. The energies of the first transition are reproduced particularly well. Thus the observation that the first two transitions in (V) occur at lower energies than in (IV) is well accounted for. Qualitatively,[4] (IV) may be considered as a highly folded dibenzohexaene and (V) as a similarly shaped benzo-octaene.

APPENDIX

Comparison of Relative Energies with Thermochemical Values.—At the suggestion of a referee a comparison is made of EH ground state energies of (II) and of (IV) with values deduced from thermochemical data. The required data (in kJ mol^{-1}) are taken from Tables 9.1, 9.2, and 9.3 of ref. 22.

The bond contributions to heats of combustion are: C–C, 206.6, C=C in *cis*-1,2-disubstituted ethylene in six-membered ring, 491.9 kJ mol^{-1}. The resonance energies (RE) are: benzene, 150.8, naphthalene, 255.6 kJ mol^{-1}. The excess RE of *trans*-stilbene is 29.3 kJ mol^{-1}. The RE of polyene is 12.6 kJ mol^{-1} per pair of interacting double bonds. In the process (I) → (II) or (III) → (IV) the number of C–C bonds increases by two but the number

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[22] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, ch. 9.

of C=C bonds decreases by one. These changes as well as the RE changes have to be taken into account. Thus the energy (E, thermochemical) of (II) relative to (I) is according to these data, $E_{(II)} - E_{(I)} = 2 \times 206.6 - 491.9 + 2 \times 150.8 + 29.3 - 5 \times 12.6 = 188.1$ kJ mol^{-1}. For purposes of comparison with the EH value (122 kJ mol^{-1}), the thermochemical value has to be slightly reduced in order to take into account the nonplanarity and the H(6)-H(6′) repulsion in (I).

The energy (thermochemical) of (IV) relative to (III) may be similarly estimated as $E_{(IV)} - E_{(III)} = 2 \times 206.6 - 491.9 + 2 \times 255.6 - 2 \times 150.8 + 29.3 - 5 \times 12.6 = 95.9$ kJ mol^{-1}. The EH value is 227 kJ mol^{-1}. Part of the difference could possibly be attributed to the H(9)-H(28), H(9)-H(30), and H(1)-H(28) repulsions, all larger in (IV) than in (III). Their contribution has to be added to the thermochemical estimate. As mentioned above, a value of 109 kJ mol^{-1} is obtained for this contribution by the strain energy calculations. The thermochemical data indicate that a large part of the energy differences $E_{(II)} - E_{(I)}$ and $E_{(IV)} - E_{(III)}$ is due to loss of resonance energy.

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