Radical Anions of Saturated Pericyclic Naphthalenes

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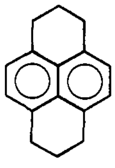
Abstract: The proton esr splittings for several pericyclic naphthalenides are reported, and the determination of conformations of these compounds through use of β splittings is discussed. In contrast to a previous report, the spin density at the alkyl-substituted positions is insensitive to peri strain, although large angle deformations at the C_β–H_b bonds are detected. A 1.2-G, δ splitting was observed for naphtho[1′,8′]tricyclo[4.3.0.0^{5,9}]non-2-ene and is discussed in terms of mixing of a filled cyclobutane orbital with the highest occupied MO of the naphthalenide system.

Pericyclic naphthalene radical ions have received a great deal of study by esr spectroscopy,[1] including many studies of anisotropic line broadening because of ion-pairing phenomema. The discovery that ring flipping of the peri-6 rings of hexahydropyrene (**1**) anion was slow on the esr time scale at low temperatures, causing different coupling constants to be observed for pseudoaxial and pseudoequatorial methylene hydrogens, as well as the appearance of two slightly different spectra for the "chair" and "boat" forms,[2] was an early conformational analysis by esr spectroscopy.[3] Considerable attention has been devoted to the broadened spectra observed at intermediate flipping rates,[1] and recently the activation energies for ring flipping of $\mathbf{1}\cdot^-$ and $\mathbf{2}\cdot^-$ were calculated to be about 6.4 and 7.9 kcal/mol, respectively, by comparison of the experimental spectra with calculated ones.[4] The low-temperature spectrum of $\mathbf{2}\cdot^-$ was subjected to conformational analysis[5] by using the simplest form of the usually accepted β-coupling equation

$$a(H_\beta) = (B_0 + B_2 \cos^2 \theta)\rho_\alpha^\pi \qquad (1)$$

where $B_0 = 0$, and a 120° phasing angle ϕ ($\theta_2 = 120° + \phi$), where θ_i is the dihedral angle between the C_β–$H_{\beta i}$ bond and the p orbital on the spin-bearing (α) carbon. The interpretation was[5] that the naphtho[1′,8′]-cycloheptene (peri-7) rings exist in the syn conformations (**3**), with $\theta_1 = (-)49°$, $\theta_2 = 71°$ (see **4**), and with a ρ_α^π of 0.31, compared with 0.17 for $\mathbf{1}\cdot^-$. This result suggests that ρ_α^π is a sensitive indicator of peri interactions.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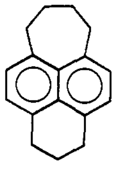
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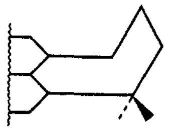
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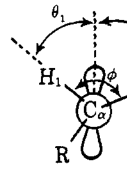
We wish to report here the synthesis of several pericyclic naphthalene derivatives, and an esr study of the effect of peri-ring size upon the splittings and conformations of such compounds which offers a reinterpretation of the previous studies[4,5] on *peri*-naphtho[1′,8′]-cycloheptenes.



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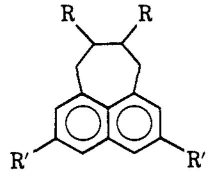
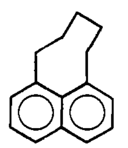
Synthesis

For our esr studies, we wished to extend the range of available pericyclic naphthalenes from the known acenaphthene (**5**), perinaphthane (**6**), and pleiadane (**7**) systems to larger ring sizes. We prepared pleiadane (**7A**), 3,6-di-*tert*-butylpleiadane (**5B**), naphtho[1′,8′]-cyclooctene (**8**), and 1-oxanaphtho[1′,8′]cyclooct-4-ene (**9**) by catalytic hydrogenation of the bis-unsaturated compounds **10A**,[6] **10B**,[7] **11**,[7] and **12**,[7] which were obtained by thermal cleavage of the appropriately substituted acenaphthene derivatives, as described elsewhere.



7A, R = H; R′ = H
B, R = H; R′ = *tert*-butyl
C, R = CH$_2$; R′ = H
D, R = CH$_2$CH$_2$; R′ = H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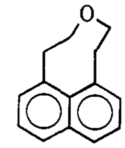

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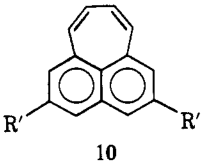

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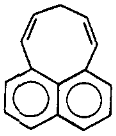
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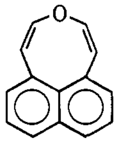

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Since **10** and **12** were observed to reduce to $\mathbf{7}\cdot^-$ and $\mathbf{9}\cdot^-$, respectively, with sodium–potassium alloy in degassed esr tubes, we did not isolate the peri-9 and peri-10 hydrocarbons directly, but formed $\mathbf{13}\cdot^-$ and $\mathbf{14}\cdot^-$ *in*

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(1) A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

(2) (a) E. de Boer and A. P. Praat, *Mol. Phys.*, **8**, 291 (1964); (b) M. Iwaizumi and T. Isobe, *Bull. Chem. Soc. Jap.*, **38**, 1547 (1965).

(3) (a) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967); (b) G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, **89**, 6536 (1967).

(4) (a) R. F. C. Clairidge, B. M. Peake, and R. M. Golding, *J. Magn. Resonance*, **6**, 29 (1972); (b) F. W. Pijpers, M. R. Arick, B. M. P. Hendricks, and A. E. deBoer, *Mol. Phys.*, **22**, 736 (1971).

(5) R. F. C. Clairidge, D. R. A. Leonard, and B. M. Peake, *ibid.*, **19**, 737 (1970).

(6) J. Meinwald, G. E. Samuelson, and M. Ikedo, *J. Amer. Chem. Soc.*, **92**, 7604 (1960).

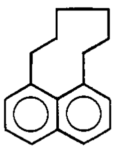
(7) S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, **95**, 1874 (1973).

Table I. Esr Splitting Constants for Pericyclic Naphthalene Radical Anion[a]

Radical anion of	Solv[c]	LW[b]	Temp, °C	*p*	*m*	*o*	β	γ	Other
5[d]	A		−80	4.17	2.42	1.04	7.53 (4 H)		
26	A	0.05	−30	4.20	2.43	1.12	6.92	0.14, 0.27	
26	B		−55	4.25	2.30	1.12	6.49	0.10, 0.27	
27	A	0.10	−45	4.18	2.48	1.11	6.60	0.28 (4 H)	
25	A	0.10	−70	4.29	2.41	1.20	6.28	0.24	0.25 (1 H)
6[e]	A		−70	4.63	1.96	1.57	8.85, 2.35	0.54, 0.37	
18	A	0.09	−40	4.89	2.11	1.50	0.19	0.93, 0.64	
24	A	0.09	−40	4.51	2.10	1.48	0.18	0.74	1.20 (4 H)
7A[e]	A		−70 (?)	5.64	1.80	1.58	6.79, 1.22	0.22 (4 H)	
7B	C	0.14	−84	4.36		1.53	7.02, 1.19	0.57, 0.24	
7D[f]	A	0.14	−65	4.67	1.90	1.64	6.32, 0.55		
7C	A	0.07	−10	4.68	1.84	1.71	6.65, 0.45	0.15	
8	B	0.07	−70	4.79	1.84	1.67	4.30, 0.57	0.57, 0.29	
9	A	0.20	−40	4.89	1.97	1.66	4.16, 0.59	0.59. 0.30	
13[f]	A	0.10	−40	4.64	1.90	1.63	6.32, 0.57	0.57, 0.29	
14[f]	A		−50	∼4.64	∼1.90	∼1.65	∼6.55, ∼0.61	Unknown	
28	A	0.11	−50	4.74	1.79	1.64	2.43 (4 H)		
29[g]	A			4.73	1.70	1.70	4.61 (6 H)		

[a] Na, K reductions. Unless otherwise noted, splittings correspond to 2 hydrogen triplets. [b] Line width used in simulation. [c] Solvents: A, THF; B, THF + 10% HMPA; C, 2:1 DME-2-MeTHF. [d] I. P. Colpa and E. deBoer, *Mol. Phys.*, **7**, 333 (1967). [e] Reference 4. [f] Never isolated neutral hydrocarbon. Generated by *in situ* reduction of the diene. For a summary of reported splittings for **29**, see R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, **51**, 1765 (1969). [g] F. Gerson, B. Weidmann, and E. Heilbronner, *Helv. Chim. Acta*, **47**, 1951 (1964).

situ from the respective diolefins. The preparation of two isomers of **15** by reaction of the bis-Wittig reagent from 1,4-dibromobutane with 1,8-naphthaldehyde has been previously reported;[8] we used the stabler cis–cis isomer in this work.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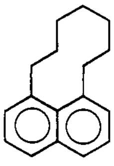
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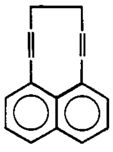
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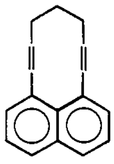
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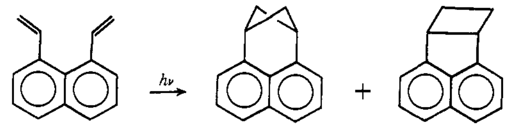
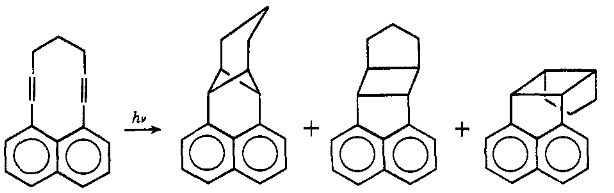
The reaction of the Wittig reagent from 1,5-dibromopentane and 1,8-naphthaldehyde gave a low yield of a mixture of isomers of **16** as the only isolated hydrocarbon product, but we have as yet been unsuccessful at separating this mixture. In our hands, the bis-Wittig route proved completely unsuccessful for preparation of **11** or the next higher homolog of **16**.

We desired derivatives of 1,8-dialkylnaphthalenes in which a C_β–H_β[9] bond was held in the plane of the naphthalene ring, to eliminate the $B_2 \cos^2 \theta$ term from the expression for a_1 (eq 1). The recent synthesis by Meinwald and Young[10] of naphtho[1′,8′]bicyclo[3.1.1]hept-2-ene (**18**) by photolysis of 1,8-divinylnaphthalene (**17**), which gives a 10:1 mixture of **18**:**19**, was therefore particularly welcome.

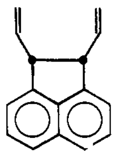


17 18 19

Photolysis of our mixture of **16** isomers gives a mixture of three compounds, shown to be **19**, **20**, and **21** from spectral data, in 2.4:5.6:1 ratios (by vpc). **20** was formed, and in nearly quantitative yield, when **16** was pyrolyzed near 400°. Similarly, the "criss-cross" adduct **24** was formed in good conversion upon pyrolysis of **23**, which apparently reverse-Cope rearranges to **15** isomers, and cycloadds like **16** and **17**.[8] Not surprisingly, photolysis of **23** gives no products derived from **15**; the adduct **25** was the sole monomeric product observed.



16 20 21 22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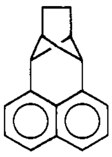
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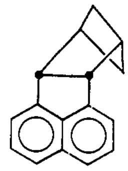
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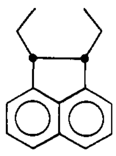
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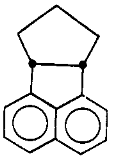
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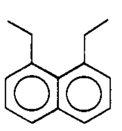
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We prepared compounds **26–28** by catalytic hydrogenation.

Esr Spectra

The esr spectra of a number of pericyclic naphthalenes have been determined, and the splittings observed ap-

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(8) S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, **94**, 6238 (1972).

(9) To avoid using two sets of nomenclature we are using the common esr nomenclature, in which an α hydrogen is one attached to an unsaturated center, β hydrogen is one carbon removed, etc., throughout. Unfortunately, this nomenclature is not consistent with usual practice in organic chemistry.

(10) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 725 (1971).

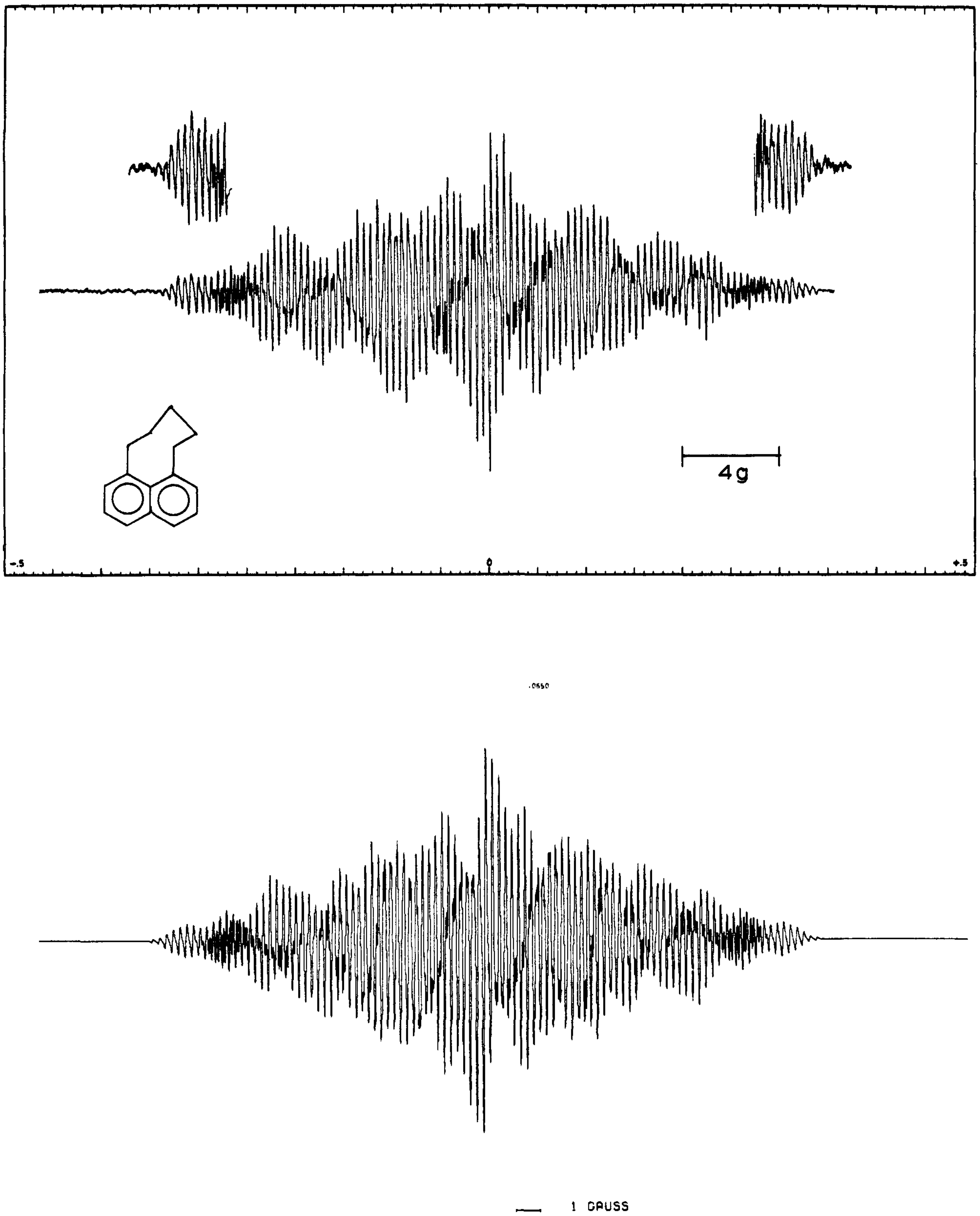


Figure 1. The esr spectrum of $8\cdot^-$ and a simulation using the parameters of Table I.

pear in Table I. Our data for previously reported radical anions, such as those from acenaphthene (**5**), perinaphthane (**6**), and pleiadane (**7A**), agreed well with the published values, which are quoted in the table. Most of our work was done with sodium–potassium alloy in THF, but in cases where ion-pairing phenomena obscured the splittings too much, we used added HMPA to increase exchange rates, and employed dimethoxyethane–2-methyltetrahydrofuran mixtures if particularly low temperatures were required.

The ring splittings were assignable on the basis of analogy, for they are quite constant for the peri-6 through peri-9 compounds studied. Our data for the anions from **29**, **5**, and **7A** agreed well with the litera-

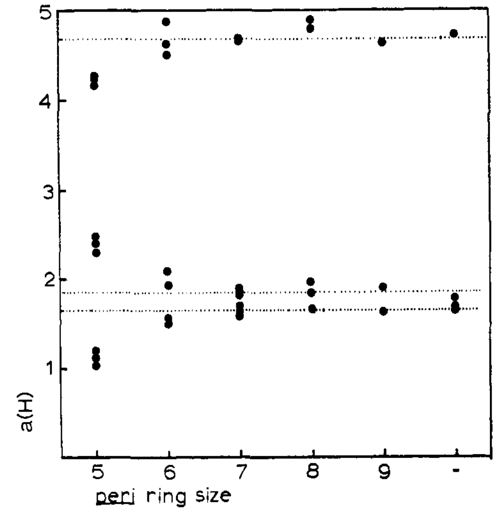


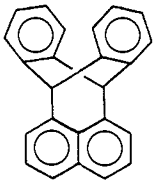
Figure 2. Naphthalene ring hydrogen esr splitting constants, displayed as a function of peri ring size. The horizontal lines are only intended as a guide for the eye.

ture, and disappearance of the intermediate-sized ring splitting for **7B** proved that the literature assignment for meta splitting of **7A** is indeed correct. A sample spectrum and simulation appears as Figure 1. We have not proven that the smaller β splittings reported are not transposed with the γ splittings of about half their size (compounds **8**, **9**, and **13**), but even if error has been made, this does not affect the calculated geometries substantially.

The first point we wish to make about the data of Table I is that the naphthalene ring splittings show little variation with ring size, except for the two-carbon (peri-5) bridge (see Figure 2). Although acenaphthylenes are easily distinguished from other 1,8-dialkylnaphthalenes, peri-6 to peri-10 compounds gave nearly identical ortho, meta, and para splittings. This constancy of splitting constant (and hence spin density) at three of the four naphthalene ring carbons which are not on the symmetry node is excellent evidence that the remaining, alkyl-substituted carbon (which we shall refer to as C_α) is also fairly constant in pericyclic and 1,8-dialkylnaphthanes. The dimethyl compound **29** gives our most reliable estimate of ρ_α^π, since the methyl groups should have $\langle\cos^2\theta\rangle$ values close to 0.5.[1] Rather arbitrarily choosing to evaluate $Q(CH_3)$ using Fessenden and Schuler's estimate[11a] of $\rho_\alpha^\pi = 0.919$ for ethyl radical, we obtain $\rho_\alpha^\pi = 0.16$ for $29\cdot^-$, and the other 1,8-dialkylnaphthalene compounds must have similar values, because of the constancy of ring splitting constants. Fraenkel and coworkers[11b] argue for ρ_α^π of $29\cdot^-$ in the range 0.18–0.19 by comparison of esr data and calculations for a series of methylated naphthalenes.

Conformational Geometries Using Esr

Geometries of radicals have often been estimated by use of eq 1, since the ratio of splittings for nonequivalent methylene hydrogens eliminates the ρ_α^π term, and if the phasing angle ϕ is assumed, θ_1 and θ_2 are easily calculated. Although B_0 is usually set equal to zero,[3] Bauld and coworkers[12] have emphasized that B_0 is usually not negligible, and from the temperature variation of β splittings, have estimated B_0/B_2 for the isopropyl group to be $+0.119$,[12a] and for the cyclopropyl group, -0.043.[12b] The dependence of calculated geometry as a function of a_1/a_2 ratio upon various B_0/B_2 values is indicated in Figure 3; substantial changes in calculated θ values are apparent for large a_1/a_2 ratios. Using compound **30**, a 1,8-dialkylnaphthalene with θ constrained to be 90°, Allendoerfer, Gallagher, and Lansbury[13] observed a β splitting corresponding to $B_0/B_2 = 0.023$, and the splitting for $24\cdot^-$ corresponds to $B_0/B_2 \leq 0.02$. Use of a low value for B_0/B_2 is most consistent with the rest of our data also,[14] and we list the calculated geometries for several pericyclic naphthalenes in Table II.



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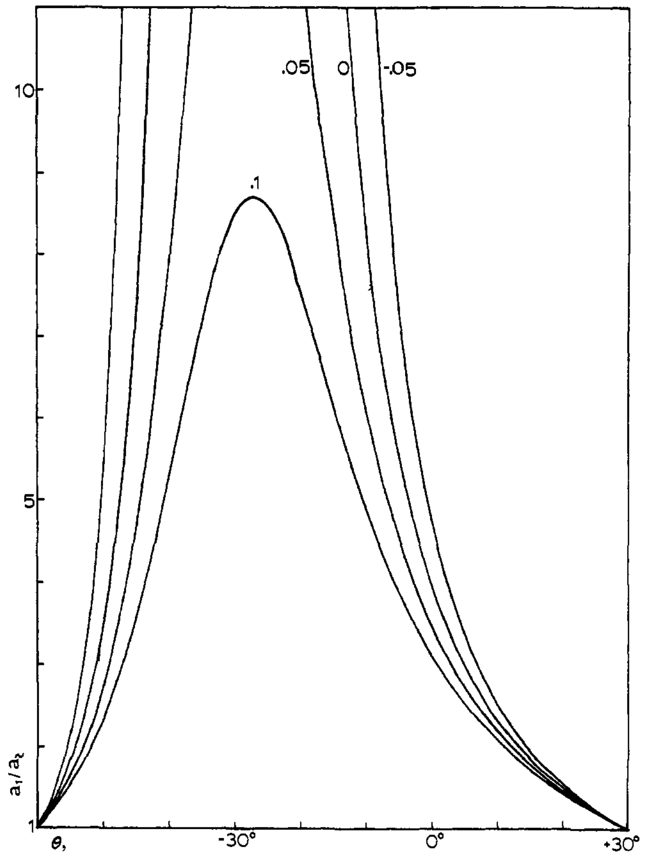

Figure 3. Plots of a_1/a_2 (the ratio of the larger β-hydrogen splitting constant to the smaller) *vs.* θ_1 (H_1–C_β–C_α–p-axis dihedral angle) for B_0/B_2 values from -0.05 to $+0.10$.

For the peri-7 compound, $7A\cdot^-$, Clairidge and co-

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[11] (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) see footnote *e*, Table I.

[12] (a) N. C. Bauld, S. E. Hudson, and J. S. Hyde, *J. Chem. Phys.*, **54**, 1834 (1971); (b) N. C. Bauld, *et al.*, *J. Amer. Chem. Soc.*, **91**, 6666 (1969).

[13] R. D. Allendoerfer, P. E. Gallagher, and P. T. Lansbury, *ibid.*, **94**, 7702 (1972).

[14] Allendoerfer and coworkers,[13] by assuming B_0 and B_2 for **29** were the same as for **7A**, calculated B_0/B_2 of **7A** as being 0.169. This value seems unreasonably high, since the maximum a_1/a_2 ratio possible is 5.62, and we observe 5.57 for **7A**, 5.90 for **7B**. As seen in Table II, use of the low B_0/B_2 value gives consistent ρ_α^π values/for **7A**–**C**.

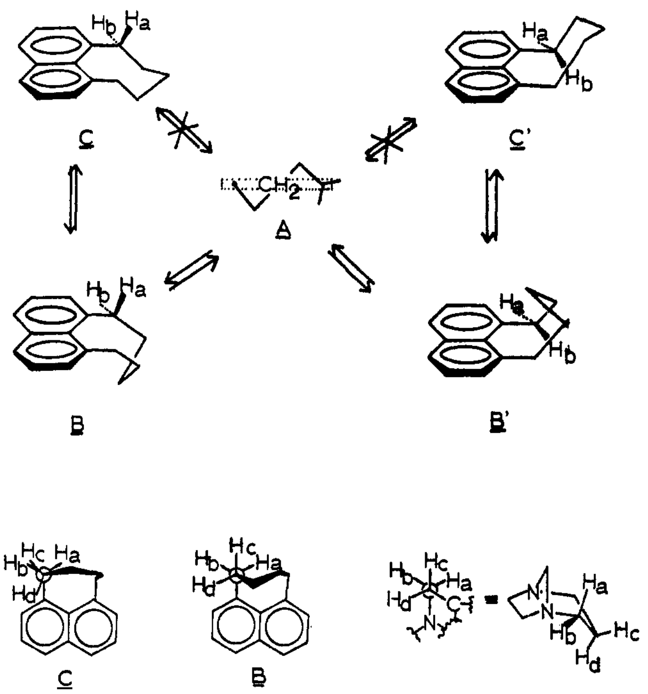


Figure 4. Pathways for interconversion of the anti (A), boatlike (B), and chairlike (C) conformations of **8**, and Newman projections for B and C, compared with 1,5-diazabicyclo[3.2.1]octane.

Table II[a]

Compd	Peri ring size	θ_1, deg	ρ_α^π
6$\cdot^-$	6	+2	0.15
7A$\cdot^-$	7	−14	0.13
7B$\cdot^-$	7	−14	0.12
7C$\cdot^-$	7	−16	0.12
8$\cdot^-$	8	−43	0.14
13$\cdot^-$	9	−16	0.12

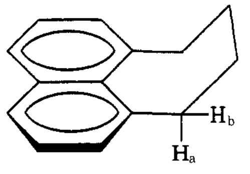
[a] θ_1 values determined from a_1/a_2, $\phi = 120°$, $B_0/B_2 = 0.02$.

workers[5] selected the −47° solution to the observed a_1/a_2 ratio, pointing out that the θ_1 angle so obtained is close to the −42° calculated if peri interaction is ignored. Allendoerfer and coworkers[13] list $\theta_1 = (-)24°$, which is the same as selecting the other solution from the a_1/a_2 plot. The latter is clearly the correct solution, since ρ_α^π is unreasonably large for the −47° solution, and θ_1 cannot reasonably be more negative for **7**$\cdot^-$ than for **8**$\cdot^-$. The large negative θ_1 solution was selected for **8**$\cdot^-$ (Table II) on the basis of a more reasonable ρ_α^π ($\theta_1 = -9°$, $\rho_\alpha^\pi = 0.075$ is the second solution). For the peri-9 case, **13**$\cdot^-$, the small, negative θ_1 value is consistent with an anti conformation, in contrast to the syn conformations of **7** and **8**. This is quite reasonable, since there are now enough methylene groups to bridge an anti conformation, and the syn conformation would be strongly destabilized by the peri interaction.

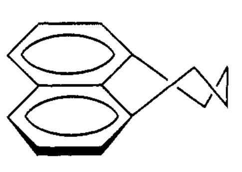
Nmr Spectrum of 8

To check the reasonability of the esr-derived conformation for **8**$\cdot^-$, we have used nmr spectroscopy on the neutral compound. At 43°, the nmr spectrum of **8** consists of the naphthalene absorptions, a broad absorption at δ 3.26 for the benzylic hydrogens (4 H), a pentet at 1.90 ($J = 6.5$ Hz, 4 H), and a multiplet at 1.31 (2 H). When the temperature is lowered to −70°, all of the aliphatic multiplets are changed, the most striking effect being to separate the benzylic hydrogens into two patterns, a doublet of doublets of doublets at 4.0 ($J \sim 14$, 12, and 7.5 Hz, H_a), and a narrower doublet of doublet of doublets at 3.0 ($J \sim 14$, 6, and 2 Hz, H_b). The downfield pattern must be caused by hydrogens which point inward toward the center of the molecule, and have a steric interaction, by analogy with the work of Lansbury and coworkers[15] on benzodihydropleiadiene derivatives. The geometrical changes associated with interconverting H_a and H_b are shown in Figure 3. Examination of models will show that the most feasible pathway for interconversion of H_a and H_b involves rotation of one end of the peri bridge of the boatlike conformation B to give the anti-alkyl conformation A as an intermediate. This rotation is not geometrically possible from the chairlike conformation C. Although A is conceivable as the stablest conformation (but a model appears far more strained than B or C), it can be ruled out because A contains a C_2 axis of symmetry, which would require that the upfield two-hydrogen multiplet be temperature independent; it is not. Choice between conformations B and C for the major conformation of **8** can be made on the basis of coupling constants. The downfield resonance (H_A) has two large splittings, 14 and 12 Hz, which must be caused by one geminal splitting and one vicinal splitting. The dihedral angle for the vicinal splitting must be close to 0 or 180° to be so large. If c were the correct conformation, the dowfield proton would be H_B. As Lansbury's work has shown, such an assignment is not reasonable. The predominance of conformation B over C is also intuitively reasonable, since B lacks the eclipsing interactions present in C. The observed coupling constants for **8** are very similar to those for the analogous positions of 1,5-diazabicyclo[3.2.1]octane[16] (Figure 4), which have a very similar geometry to B, as is shown next to the structure. The $\Delta G^\ddagger$ for interconversion of H_A and H_B was crudely estimated by using the approximate expression[16] $\Delta G^\ddagger(T_c) = 4.57T_c[9.67 + \log (T_c/\Delta\delta_{ab})]$. This gave $\Delta G^\ddagger(30°) = 14.0$ kcal/mol for **8** and $\Delta G^\ddagger(25°) = 13.7$ kcal/mol for the oxo analog **9**, which had a completely analogous temperature-dependent nmr spectrum.

As with **8**, both syn and anti alkyl conformations are possible for **7**, but the transition state for interconverting them must be far lower than for **8**, since the nmr signals for H_a and H_b remain rapidly exchanging to −70°. From the substantial similarity of the esr spectra of **7A**$\cdot^-$, **7C**$\cdot^-$, and **7D**$\cdot^-$, it seems likely that the syn conformation predominates, since the latter two compounds are frozen in this conformation by the fused ring. The calculated θ_1 values for both **7**$\cdot^-$ and **8**$\cdot^-$ are considerably less negative than models ignoring



7 syn



7 anti

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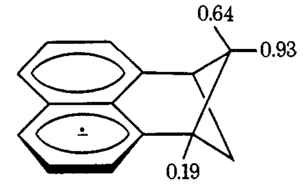
[15] J. G. Colson, P. T. Lansbury, and F. D. Saeva, *J. Amer. Chem. Soc.*, **89**, 4987 (1967), and references therein.

[16] S. F. Nelsen and P. J. Hintz, *ibid.*, **94**, 7105 (1972).

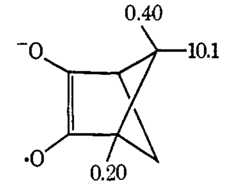
peri interactions predict; we suggest that the interaction does cause considerable outward bending at the interacting carbons.

Long-Range Splittings

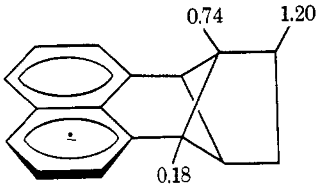
The γ-hydrogen splittings shown in Table I do not yield much structural information. We note that even in the case of diethylacenaphthene anion, **26**$\cdot^-$, where rotation of the ethyl groups should be taking place, different γ splittings for the two pairs of diastereotopically nonequivalent hydrogens were observed. In contrast, the rigidly held and obviously nonequivalent γ hydrogens of **27**$\cdot^-$ did not give observably different splittings.



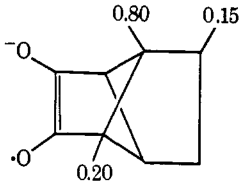
18$\cdot^-$



18S$\cdot^-$



24$\cdot^-$



24S$\cdot^-$

The long-range splittings of the 1,3-disubstituted cyclobutane derivatives (**18**$\cdot^-$ and **24**$\cdot$)$^-$ are particularly interesting when compared to those of the related semidiones, which have been reported by Russell and coworkers.[17] The far greater exo splitting for the semidione compared to the naphthalenide **18**$\cdot^-$ is expected, since the C_γ–H_X bond lies in the nodal plane of the naphthalenide system, cancelling out the "W-plan" contribution to the splitting. Almost as dramatic, however, is the eightfold larger δ splitting of **24**$\cdot^-$ compared with **24S**$\cdot^-$. The α-spin density of the semidione is believed to be slightly higher than that of the naphthalenide system,[3b] and is certainly not eight times less. Hoffmann and Davidson[18] have recently discussed the valence orbitals of cyclobutane in terms of a Walsh-like model, and pointed out that very little experimental evidence is available for conjugative interactions of cyclobutane rings. We suggest that the δ splitting of **24**$\cdot^-$ is an outstanding example of such an effect. A simplified interaction diagram for the cyclobutane ring with the highest occupied MO of the naphthalenide and semidione systems is shown in Figure 5. The A_2 cyclobutane orbital is of the proper symmetry to mix with the naphthalene HOMO, which would lead to unusually large spin densities in the cyclobutane carbon–carbon bonding orbitals, having the symmetry shown in structure **30**. If p orbitals at the γ carbons parallel to the naphthalene contained excess spin, the 1.2 G $a(H_\delta)$ observed would be estimated to require a ρ_α^π of 0.027 (1.2/[58.4(0.75)]), or about 17% that of ρ_α^π. The orbitals at C_γ are not actually pure p orbitials, as is shown in structure **31**, but a substantial interaction of the naphthalene and cyclobutane orbitals is indicated by the large δ splitting observed. The only other observable δ splitting was a tiny one for one of the hydrogens of **23**. Since one of the hydrogens is held close to the naphthalene ring, as indicated by the nmr spectrum (see Experimental Section), a through space interaction seems likely.

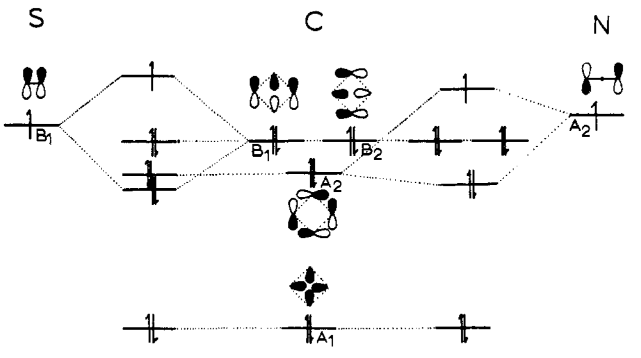
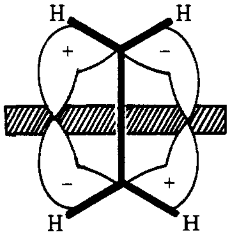


Figure 5. Interaction diagram showing allowed mixing of the filled cyclobutane (C) orbitals with the highest occupied MO's of a semidione (S, left) and naphthalenide (N, right) system held in the geometry of **24S** and **24**. Only the π orbitals at C_α are shown for the semidione and naphthalenide π systems.



We were unable to observe well-resolved spectra from **20**$\cdot^-$ but whether the problem was freezing cyclohexane ring inversion, which destroys the C_2 axis of the molecule and results in many different splittings, or intermediate flipping rates which broadened the lines was not ascertained.

Experimental Section

General Comments. Spectra were recorded on Beckman IR-8, Cary 15, Varian A-60A, HA100, or XL100, E-15, and AEI MS-902 instruments. The pyrolysis apparatus has been previously described.[7]

Pleiadane (7a). Pleiadiene (90 mg) in 3 ml of absolute ethanol was added to a suspension of 80 mg of prereduced (0.5 hr) 10% Pd/C in 10 ml of absolute ethanol. Filtration of the solution and rotovaporation yield a colorless solid which was sublimed, yielding 88.2 mg (94%) of pleiadane: mp 57–58° (lit.[9] 57–58°; nmr δ ($CDCl_3$) 2.02 (m, 4 H), 3.23 (m, 4 H), 7.05–7.75 (m, 6 H); ir 3.26, 3.28, 3.39, 3.48, 6.31, 6.86 μ; uv λ_{max} nm (log ϵ) 225 sh (4.89), 228 (4.99), 245 (3.26), 267 sh (3.71), 276 (3.90), 286 (3.98), 293 sh (3.86), 306 (3.32), 321 (3.18).

6,9-Di-*tert*-butylpleiadane (7B) was prepared by catalytic hydrogenation of **10B**[7] (10% Pd/C, ethanol, 2.06 equiv of H_2 consumed). The yield was 90 mg (96.4%): mp 114–115.5°; nmr δ 1.35 (s, 18 H), 2.02 (m, 4 H), 3.20 (m, 4 H), 7.20 (d, J = 2 Hz, 2 H), 7.40 (d, J = 2 Hz, 2 H); ir 3.37, 3.39, 3.43, 3.48, 6.19, 6.26, 6.79, 6.86, 7.20, 7.37, 7.87 μ; uv λ_{max} nm (log ϵ) 230 (4.82), 235 (4.95), 284 (3.74), 323 (2.79). *Anal.* Calcd for $C_{22}H_{30}$: C, 89.72; H, 10.26. Found: C, 89.87; H, 10.09.

Naphtho[1′,8′]cyclooctene (8) was prepared by catalytic hydrogenation of **11**[7] (10% Pd/C, ethanol, 2.8 equiv of H_2 consumed). Tlc (silica gel, PF_{254}, 12.5% $AgNO_3$, benzene, 1×, R_f 0.5) gave, after sublimation, 75 mg (94%): mp 55–56°; nmr δ ($CDCl_3$, XL-100, +50°) 1.32 (m, 2 H), 1.89 (m, 4 H), 2.24 (m, 4 H), 7.14–7.79 (m, 6 H); ir 3.32, 3.41, 3.51, 6.29, 6.94, 7.95 μ; uv λ_{max} nm (log ϵ) 223 (5.03), 228 (5.20), 245 sh (3.32), 267 sh (3.73), 276 (3.93), 286

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(17) G. A. Russell, R. R. Whittle, and R. G. Keske, *ibid.*, **93**, 1467 (1971).

(18) R. Hoffmann and R. B. Davidson, *ibid.*, **93**, 5699 (1971).

(4.03), 293 sh (3.86), 303 (3.87), 306 (3.29), 316 (3.02), 321 (3.08). *Anal.* Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.21. Found: C, 91.93; H, 8.16.

1,5-Naphtho[1′,8′]-3-oxapentane (9) was prepared by catalytic hydrogenation of **12**[7] (10% Pd/C, ethanol, 1.0 equiv of H_2 consumed). Sublimation gave 78 mg (97.5%): mp 101–102°; nmr δ ($CDCl_3$, XL-100, +43°), 2.53 (m, 4 H), 3.96 (t, $J = 6$ Hz, 4 H), 7.14–7.78 (m, 6 H); ir 3.28, 3.33, 3.38, 3.42, 3.51, 8.40, 9.08 μ; uv λ_{max} nm (log ϵ) 224 sh (4.78), 228 (3.93), 245 sh (3.15), 265 sh (3.59), 273 (3.78), 288 (3.82), 291 (3.71), 296 (3.71), 304 (4.04), 390 (2.75), 314 (2.75), 318 (2.66); exact mass 198.1050 (calcd for $C_{14}H_{14}O$, 198.1045).

Naphtho[1′,8′]tricyclo[4.4.0.$0^{5,10}$]dec-2-ene (20). Pyrolysis[8] of **16** at 430° (2.5 sec) gave 38 mg (95%) of **20** which was sublimed: mp 60–61°; nmr δ 2.02 (m, 6 H), 2.50 (broad s, 2 H), 3.25 (s, 2 H), 7.85–8.15 (m, 6 H); ir 3.28, 3.41, 3.49, 6.23 μ; uv λ_{max} nm (log ϵ) 228 (4.40), 236 (4.30), 272 sh (3.42), 279 (3.62), 290 (3.72), 302 (3.54), 307 (3.39), 316 (2.81), 321 (2.87); exact mass 220.1250 (calcd for $C_{17}H_{16}$, 220.1252).

Photolysis of 16. A solution of 70 mg of **16** in 125 ml of ether was photolyzed for 2 hr, 35 min through a Vycor filter while bubbling through nitrogen. Rotovaporation of the ether yielded a yellowish solid which was prepared by vpc (FFAP, column temperature, 225°) to give the following products (compound (retention time in minutes, %)): **22** (7.6, 11) [nmr δ (C_6D_6, XL-100 Fourier transform, 450 scans, partial) 0.76–1.64 (m, 6 H), 3.08 (m, 2 H), 4.10 (m, 2 H); mass spectra *m/e* (%) 221 (P + 1, 2), 220 (P, 12), 165 (7), 152 (100); exact mass 220.1246 (calcd for $C_{17}H_{16}$, 220.1252)], **21** (9.0, 62) [nmr δ 1.3–2.1 (m, 6 H), 2.55 (m, 2 H), 4.45 (m, 2 H), 7.05–7.60 (m, 6 H); ir 3.28, 3.39, 3.50, 6.25, 7.35 μ; uv λ_{max} nm (log ϵ) 225 sh (4.76), 230 (4.94), 247 (3.12), 273 (3.65), 289 (3.89), 298 (3.93), 302 (3.74), 207 (3.70), 316 (3.13), 320 (3.19); mass spectra *m/e* (%) 221 (P + 1, 3), 220 (P, 12), 198 (28), 165 (45), 152 (100); exact mass 220.1245 (calcd for $C_{17}H_{16}$, 220.1252)], and **20** (12.3, 26).

3-Naphtho[1′,8′]cyclodeca-1,3,6-triene (16) was prepared by a bis-Wittig reaction using the Wittig reagent derived from pentamethylene bromide[19] and 1,8-naphthaldehyde, following the procedure of Stille and Foster[20] for divinylnaphthalene. Naphthaldehyde hydrate (2.3 g) and 10.3 g of phosphonium salt gave 310 mg of crude product. Tlc (silica gel PF_{254}, 12.5% $AgNO_3$, $CHCl_3$–ether 6:4, 1×) gave 160 mg (6.3%) of product (R_f 0.52). Sublimation gave a sample: mp 66–67°; nmr δ (C_6D_6, XL-100) 1.0–2.5 (m, 6 H), 4.84–5.50 (m, 2 H), 5.40–6.40 (m, about 1 H), 7.04–7.77 (m, 7 H); ir 3.25, 3.32, 3.41, 3.50, 6.95, 10.37, 12.0, 15.0 μ; uv λ_{max} nm (log ϵ) 223 (4.73), 278 sh (3.79), 287 (3.88), 2.92 sh (3.84), 297 sh (3.81); exact mass 220.1246 (calcd for $C_{17}H_{16}$, 220.1252). The product was a mixture of isomers.

***cis*-1,2-Divinylacenaphthene (23).** Using the method of Stille and Foster,[20] the ylide prepared from 23.1 g of the phosphonium salt from 1,4-dibromobutane[21] was allowed to react with 1,8-naphthaldehyde prepared *in situ* from 5.25 g of the hydrates in refluxing benzene–ether solution. After filtration, addition to 250 ml of water, and separation of the organic layer, this layer was washed with 3 × 80 ml portions of 1 *N* HCl, dried ($MgSO_4$), concentrated, and washed through a plug of alumina with pentane, giving 1.15 g of **23**: mp 79.5–80.5° (methanol); nmr δ 4.42 (broad d, 2 H), 4.95–6.20 (m, 6 H), 7.1–7.8 (m, 6 H); ir 3.24, 3.26, 3.32, 6.79, 7.0, 9.22, 9.78, 14.45 μ; uv λ_{max} nm (log ϵ) 2.18 (4.77), 229 (4.88), 266 (3.65), 277 (3.85), 288 (3.93), 299 (3.76), 205 (3.56), 315 (2.16), 319 (2.16); exact mass 206.1098 (calcd for $C_{16}H_{14}$, 206.1095).

Naphtho[1′,8′]tricyclo[4.3.0.$0^{5,9}$]non-2-ene (24) was the major product of pyrolysis of **23** by sublimation through a hot tube at 410–375°[8] and was isolated by tlc (PF_{254}, $CHCl_3$–ether 6:4, one elution); mp (sublimed material) 136–137°; nmr δ 1.97 (s, 4 H), 2.67 (s, 2 H), 2.86 (s, 2 H), 6.8–7.6 (m, 6 H); ir 3.28, 3.38, 3.42, 3.46, 6.23, 6.63 μ; uv λ_{max} nm (log ϵ) 231 (4.53), 237 (4.55), 272 (3.69), 281 (3.68), 292 (3.97), 302 (3.82), 307 (3.54), 317 (3.07), 321 (3.01). *Anal.* Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.84. Found: C, 93.09; H, 6.86.

Naphtho[1′,8′]tricyclo[5.1.1.$0^{2,6}$]non-3-ene (25). A solution of 120 mg of **24** in 250 ml of ether was photolyzed through a Vycor filter for 70 min while stirring with nitrogen. Rotovaporation of the solvent gave a very yellow residue which was determined by nmr to be 50% converted. The oil was taken up in a few drops of carbon tetrachloride and filtered through an alumina plug, eluting with pentane to give a clear oil after rotovaporation. The mixture was rephotolyzed for another 3 hr, rotovaporated, and tlc prepared (silica gel PF_{254}, 12.5% $AgNO_3$, benzene, 1×, R_f 0.7), yielding 40 mg of a colorless oil: nmr δ (C_6D_6, XL-100), 0.50 (dd, $J_{C,D} = 7.5$ Hz, $J_{C,F} = 1$ H_C), 1.14 (dd, $J_{F,E} = 6.5$ Hz, $J_{F,C} = 10$ Hz, 1 H_F), overlaps 1.15 (m, $J_{D,B} = 4.25$ Hz, $J_{D,C} = 7.5$ Hz, 1 H_D), 1.72 (dt, $J_{E,F} = 6.5$ Hz, $J_{E,B} = 2.5$ Hz, 1 H_E), 2.54 (dd, $J_{B,D} = 4.25$ Hz, $J_{B,E} = 2.5$ Hz, 1 H_B), 3.81 (s, 2H_A), 7.12–7.65 (m, 6 H);[22] ir 3.29, 3.36, 3.47, 6.18, 6.24, 7.32, 7.77, 8.05, 8.29, 8.69 μ; uv λ_{max} nm (log ϵ) 223 (4.78), 228 (4.94), 243 (3.20), 268 (3.64), 278 (3.82), 288 (3.88) 299 (3.70), 304 (3.54), 314 (2.94), 318 (2.94); mass spectra *m/e* (%) 208 (P + 2, 2), 207 (P + 1, 12), 206 (P, 60), 178 (12), 165 (100), 152 (27), exact mass 206.1100 (calcd for $C_{16}H_{14}$, 206.1095).

1,2-*cis*-Diethylacenaphthene (26) was prepared by hydrogenation of **23** (10% Pd/C, ethanol), mp 48–50°, and had spectral properties in agreement with the structure.

Naphtho[1′,8′]bicyclo[3.3.0]oct-2-ene (27) was prepared by catalytic hydrogenation of naphtho[1′,8′]tricyclo[3.3.0.$0^{6,8}$]oct-2-ene,[7] mp 66–68° (lit.[23] 68–69°), spectral data consistent.

Esr spectra were reocrded on a Varian E-15 spectrometer, and the splittings reported are based on successful simulations using the line widths of Table I. Anisotropic line broadenings were detectable in many of the spectra.

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(22) The coupling constants reported were obtained by decoupling experiments and agree well with those reported for benzobicyclo[2.1.1]-hexene: M. Pomerantz, R. N. Wile, G. W. Gruber, and U. Roy, *J. Amer. Chem. Soc.*, **94**, 2752 (1972).

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