Bond Fixation in Annulenes. 13. Kinetic Analysis of Dynamic Behavior in Peripherally Crowded Cyclooctatetraenes. Probe of the Methyl/Phenyl Dichotomy in Tetrasubstituted Derivatives[1]

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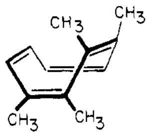
1,4-Dimethyl-2,3-diphenyl- (**5**) and 1,6-dimethyl-7,8-diphenylcyclooctatetraenes (**6**) have been prepared and found to exist in equilibrium with relatively high concentrations of the respective valence isomeric bicyclo[4.2.0]octatrienes **14** and **13**. Whereas **6** is a meso compound, **5** is chiral and has been obtained in optically active form by direct resolution with (–)-*endo*-bornyl-1,2,4-triazoline-3,5-dione (**17**). The absolute configuration of one of the urazole adducts has been established by X-ray crystal structure analysis. The rates of racemization of resolved **5** were determined. With use of samples of racemic **5** and **6**, the rates and energetics of π-bond shifting within this pair of [8]annulenes were determined. These combined kinetic studies permitted indirect assessment of the rates and activation parameters for ring inversion in **5**. These data are compared to those previously obtained for the tetramethyl congeners and the relative steric bulks of methyl and phenyl substituents thereby become apparent.

Recent investigations in this laboratory[3–6] of the ring inversion (RI) and bond shifting (BS) behavior of cyclooctatetraenes have established that proper substitution of the [8]annulene core can allow for detailed quantitative analysis of these dynamic phenomena. When three or four contiguous alkyl groups are present, the magnitudes of the barriers to RI and BS can become sufficiently elevated to allow isolation of shelf-stable pairs of bond shift isomers such as **1** and **2**. The levels of peripheral strain introduced by these substitution plans serve to impede mechanical tub-to-tub inversion through planar delocalized transition states such as **3**. The bond shifting process mediated by **4** is similarly, but not identically, disadvantaged. Although intraannular bond angles are widened in both instances (with concurrent heightened compression of the peripheral substituents), the differing annular bond lengths which distinguish **3** and **4** give rise to dissimilar energy requirements.[4–6]



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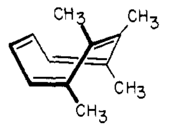

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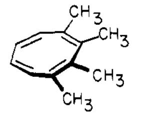

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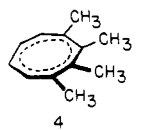

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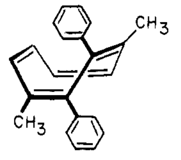
With use of our techniques, the magnitudes of $\Delta\Delta G^{\ddagger}$ which separates k_{BS} and k_{RI} in any cyclooctatetraene are determined by subtraction of two relatively small and rather accurate numbers. Because of the high reliability of the kinetic data, it has proven possible to separate general steric from buttressing effects in permethylated cyclooctatetraenes.[5] Of especial importance is the fact that the contribution of electronic factors to $\Delta\Delta G^{\ddagger}$ is made increasingly apparent as peripheral steric constraints are progressively minimized. In this context, the noncontiguously substituted 1,3-[6] and 1,4-di-*tert*-butylcyclooctatetraenes[7] have been studied in considerable detail for the purpose of amplifying our knowledge of antiaromaticity (**4** is a prototypical $4n$ delocalized system).

The present study was undertaken with a different motive in mind. The severe crowding inherent in **3** and **4** is recognized to cause $\Delta G^{\ddagger}_{25}$ for BS and RI (30.9 kcal/mol) within the tetramethyl derivative to become equal, thereby providing the first example where an energetic imbalance favoring ring inversion has not prevailed.[4,5] With replacement of the pair of internal methyl groups by phenyl as in **5** and **6**, the opportunity is made available to assess the level of steric strain due to intramolecular crowding in the planar alternate [8]annulene **7**. Furthermore, since the bond shifting pathway which interconnects **5** and **6** should be mediated by **9**, an analysis of the differences or similarities in steric interaction at the respective transition states is made possible and provides an independent probe of the relative size of methyl vs. phenyl in activated complexes of this type.



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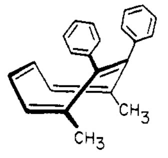

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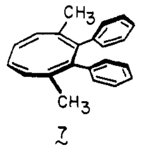

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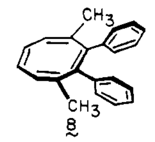

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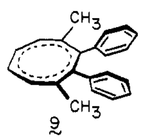

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[2] Graduate School Postdoctoral Fellow, 1979–1980.

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[7] (a) Paquette, L. A.; Hefferon, G. J.; Samodral, R.; Hanzawa, Y., paper in preparation. (b) We have learned that Professor Andrew Streitwieser has independently examined the kinetics of bond shifting of the 1,4-di-*tert*-butyl derivative.

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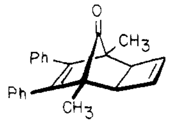
Interest in the physical properties of overcrowded molecules[8] and of the space-filling demands of aryl rings is, of course, not new. Noteworthy in this respect are the studies by Mislow and co-workers of torsional isomerism in triarylmethanes,[9] tetraarylethanes,[10] and related systems,[9,11] by House[12] and Roberts[13] of *peri*-diphenylnaphthalene derivatives, and by Gust of polyarylbenzenes and pyridines.[14] In all cases, valuable insight into the effect of intramolecular strain on ground-state structures has been gained. Invariably, the focus has been on the extent of internal mobility which can be achieved when aryl substituents are engaged in serious nonbonded repulsion. While phenyl groups are likewise brought face-to-face in 7–9 with resultant steric stress, a more fascinating and important question deals with the manner in which the combined steric crowding in these activated complexes is accommodated relative to that in their tetramethyl counterparts.

There does not exist a wealth of information concerning the relative sizes of phenyl and methyl, particularly when buttressing effects are involved as they are in the above cyclooctatetraenes. The conformational free energy difference between an axial and equatorial methyl group in cyclohexane ($\Delta G° = 1.7$)[15] indicates CH_3 to exert less repulsive energy than C_6H_5 ($\Delta G° = 3.0$) under these circumstances.[16,17] These equilibrium data have frequently been taken as an indication of the greater average steric bulk of phenyl relative to methyl in a wide range of structural environments. An early presumption that the conformational energies of methyl and phenyl should not be additive[18] has more recently been shown to be in agreement with contemporary NMR data in certain[19] but by no means all cases.[19,20] For these reasons, the recent claim by Warrener et al.[21] that **6** enters readily into bond shifting at ca. 135 °C while **2** is reluctant to do so even at 350 °C appeared quite surprising to us. Their observations were rationalized in terms of the ability of the phenyl groups to orient themselves perpendicularly to the adjoining planar [8]annulene ring, a steric relief maneuver not available to the methyl substituent. Unfortunately, the experimental technique employed by the Australian group was not mentioned. We have earlier demonstrated that **2** does, in fact, experience BS at conveniently measured rates in the vicinity of 120–160 °C.[4f,5] In an effort to clarify this issue and to develop further understanding of the methyl/phenyl dichotomy, we have undertaken a detailed kinetic analysis of the dynamic behavior of **5** and **6**, and detail our findings herein.

Results

Synthesis of the Dimethyldiphenylcyclooctatetraenes. Access to a mixture of the isomeric tricyclic ketones **10** and **11** (ca. 4:1 ratio) was gained by Diels–Alder cycloaddition of *cis*-3,4-dichlorocyclobutene[22] to 2,5-dimethyl-3,4-diphenylcyclopentadienone (generated in situ from its dimer),[23] followed by dechlorination of the adducts with zinc in hot ethanol as previously described.[24] When irradiated through quartz with 2537-Å light (Rayonet reactor) in acetone solution, **10** and **11** were subject to decarbonylation.[25] Reasonable control of the photolysis conditions was required in order to preclude operation of a secondary [2 + 2] photofragmentation which leads from **12** to acetylene and the substituted benzene.[25,26] Generally, irradiation was continued until the triene/ketone ratio approached 1:2 (ca. 3 h). When **12** was heated at 60–80 °C for several hours, an equilibrium mixture of **6** with its bicyclic valence tautomer **13** was observed.[25] At more elevated temperatures (120–130 °C, diglyme, N_2 atmosphere), a mixture of **5**, **6**, **13**, and **14** was made available. The composite ^1H NMR spectrum, as well as individual peak assignments to the four components,[27] are in full agreement with precedent.[25]



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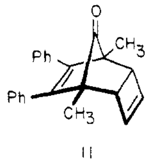

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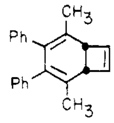

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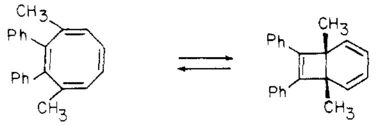

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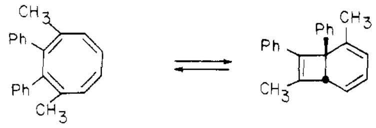

5 14

To allow for subsequent resolution studies, clean separation of the dissymmetric valence isomer pair **5** ⇄ **14** from the planar symmetric **6** ⇄ **13** was warranted as a preliminary step. The desired fractionation was conveniently achieved by addition of *N*-methyltriazolinedione and separation of the two resulting adducts (**15** and **16**) by high-pressure liquid chromatography. The individual COT

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[13] (a) Clough, R. L.; Roberts, J. D. *J. Org. Chem.* **1978**, *43*, 1328. (b) Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *Ibid.* **1976**, *41*, 3603. (c) Clough, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1018.

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[26] Warrener, R. N.; McCay, I. W.; Tan, R. Y. S.; Russell, R. A. *Tetrahedron Lett.* **1979**, 3183.

[27] **5**: δ 6.3–5.6 (m, vinyls), 1.55 (s, methyls). **6**: δ 6.3–5.6 (m, vinyls), 1.82 (br s, methyls). **13**: δ 5.77 (s, vinyls), 1.40 (s, methyls). **14**: δ 6.3–5.6 (m, vinyls), 2.05, 1.63 (br s, methyls).

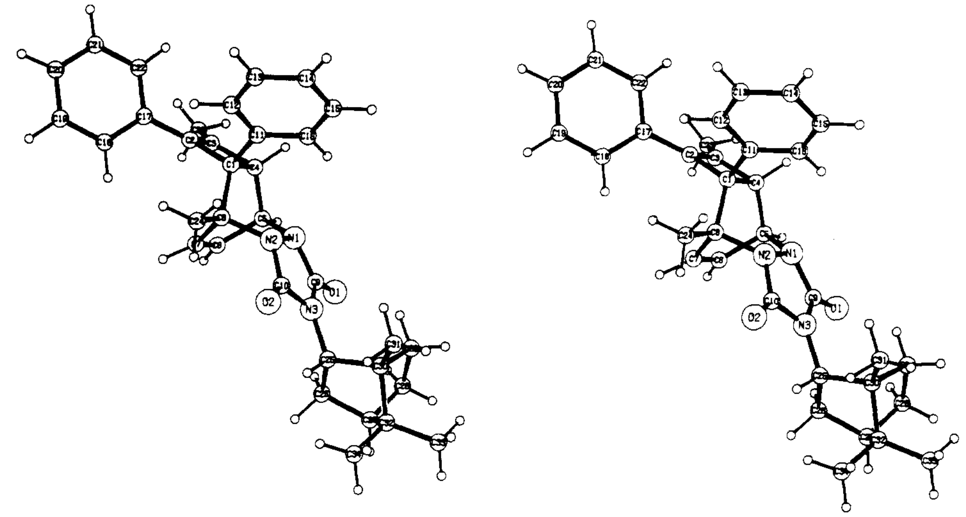
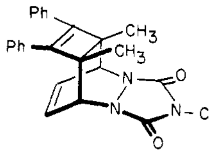


Figure 1. Three-dimensional view of (−)-19 as determined by X-ray crystal structure analysis.

bond shift isomers could subsequently be liberated by conventional hydrolysis–oxidation of the purified urazoles.



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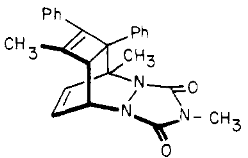

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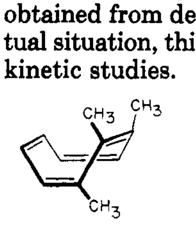
Preparation of Optically Active 1,4-Me_2-2,3-Ph_2COT and the Assignment of Absolute Configuration. Two important points emerge from the above: (a) the separation of 5 ⇄ 14 from their bond shift and positional isomers is achievable with relative ease, and (b) this cyclooctatetraene enters efficiently into [4 + 2] cycloaddition with reactive dienophiles exclusively via bicyclo[4.2.0]octatriene 14. Since adduct 16 is chiral, reaction of 5 with (−)-*endo*-bornyltriazolinedione (17)[4,6,28] should give rise to 18 and 19, diastereomers which were expected to be amenable to separation. In actuality, preparative-layer chromatography sufficed in the present instance. The purified levorotatory diastereomer, $[\alpha]^{20}_D$ −38.5° (*c* 6, C_2H_5OH), was determined to be 19 by X-ray crystal structure analysis. A stereoscopic view of the model is shown in Figure 1. Hydrolysis–oxidation of 19 gave a colorless levorotatory oil, $[\alpha]^{20}_D$ −24.3° (*c* 10, ether). Since the equilibrium mixture is not dominated by the medium-ring structure (14/5 = 1.2 at 25 °C) as in most circumstances of this type,[29] there is no guarantee that the absolute configuration indicated by formula (−)-5 in Scheme I is truly that of the levorotatory cyclooctatetraene. It is significant to note that the given designation of absolute stereochemistry conforms to that determined earlier for (−)-20,[4e] (−)-21,[4f] and (−)-22.[6a] However, whereas the present levorotatory hydrocarbon is isolated by hydrolysis of a levorotatory *endo*-bornylurazole, the other three are obtained from dextrorotatory adducts. Whatever the actual situation, this issue is not at all crucial to the ensuing kinetic studies.



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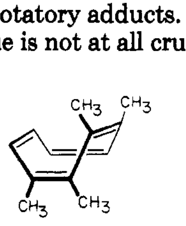

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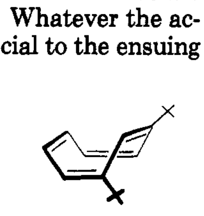

(−)-22

Table I. Activation Parameters for the Valence Isomerizations 13 → 6 and 6 → 13 (DNMR Derived from Studies Conducted at 373-413 K)[a]

for ring opening of 13	for ring closure of 6
E_a = 22.2 kcal/mol	E_a = 19.1 kcal/mol
A = 2.3 × 10^{14} s^{-1}	A = 2.2 × 10^{12} s^{-1}
$\Delta H^{\ddagger}_{25}$ = 21.6 kcal/mol	$\Delta H^{\ddagger}_{25}$ = 18.5 kcal/mol
$\Delta S^{\ddagger}_{25}$ = 5.2 eu	$\Delta S^{\ddagger}_{25}$ = −4.0 eu
$\Delta G^{\ddagger}_{25}$ = 20.1 kcal/mol	$\Delta G^{\ddagger}_{25}$ = 19.7 kcal/mol

[a] The $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values are extrapolated.

Table II. Activation Parameters for the Valence Isomerizations 14 → 5 and 5 → 14 (DNMR Derived from Studies Conducted at 373-413 K)[a]

for ring opening of 14	for ring closure of 5
E_a = 23.7 kcal/mol	E_a = 21.2 kcal/mol
A = 2.6 × 10^{14} s^{-1}	A = 7.0 × 10^{12} s^{-1}
$\Delta H^{\ddagger}_{25}$ = 23.1 kcal/mol	$\Delta H^{\ddagger}_{25}$ = 20.6 kcal/mol
$\Delta S^{\ddagger}_{25}$ = 5.4 eu	$\Delta S^{\ddagger}_{25}$ = −1.7 eu
$\Delta G^{\ddagger}_{25}$ = 21.5 kcal/mol	$\Delta G^{\ddagger}_{25}$ = 21.1 kcal/mol

[a] The $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values are extrapolated.

Isodynamical Processes in 5 and 6. The kinetic intricacies associated with ring inversion and bond shifting within optically active 5 is illustrated in Scheme II. For our purposes, k_1 shall define the rate at which (−)-5 is converted to (+)-5 by mechanical RI through planar alternate transition-state 7. When the optically active COT acquires energy adequate to experience bond shifting (thus involving 9), we presume that (−)-5 will transmute not only into 6 but into (±)-5 as well. The rate of this process, defined as k_2 also includes the operation of concurrent BS and RI (slanting arrows in Scheme II). Finally, the reconversion of *meso*-6 to (±)-5 must be considered. This reverse rate, k_{-2}, need not be identical with the forward rate because of the obvious structural differences in the two bond shift isomers.

Understandably, analysis of the preceding kinetic profile becomes feasible only if the rates at which 5 and 6 experience valence isomerization with bicyclo[4.2.0]octatrienes 14 and 13, respectively, are much faster than k_1, k_2, and k_{-2}. For this reason, these rates were evaluated first. The results, obtained by DNMR methods[30] and summarized in Tables I and II, show the free energies of activation

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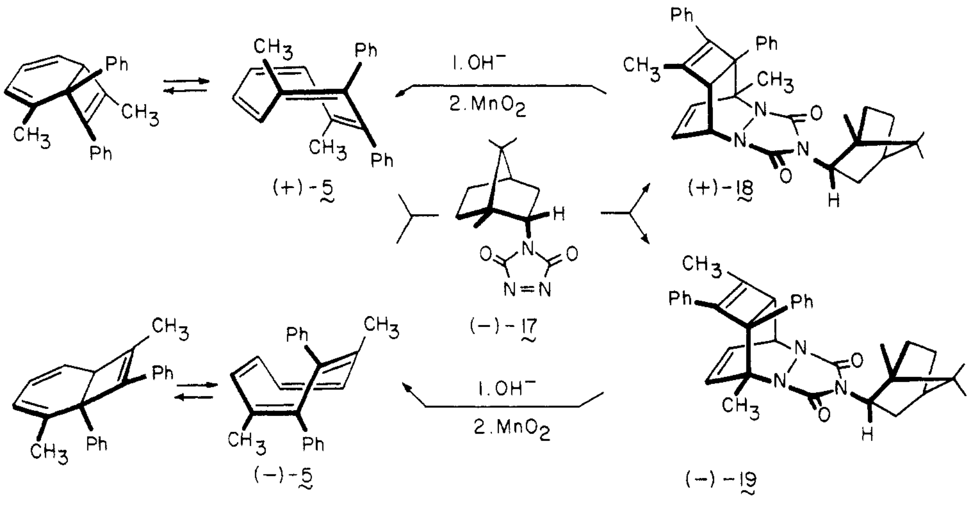
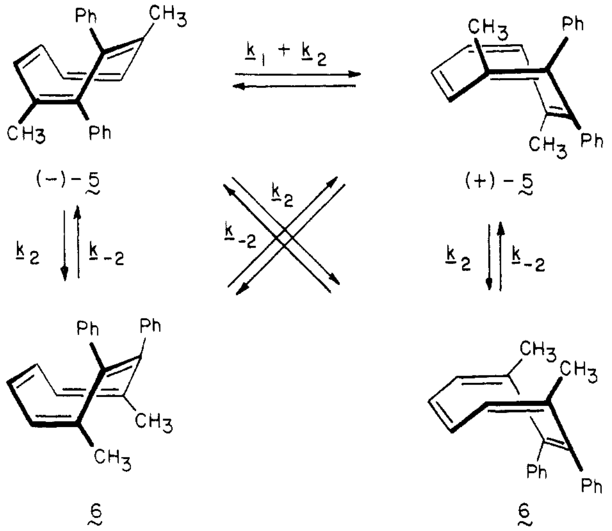
[29] Paquette, L. A. *Tetrahedron* **1975**, *31*, 2855.
[30] The DNMR program was provided to us by Professor Gideon Fraenkel of this department.

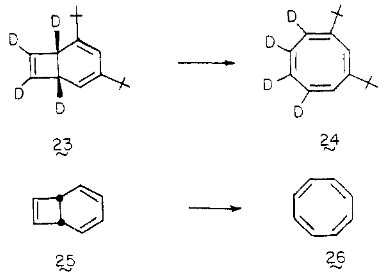
Scheme I



Scheme II



($\Delta G^{\ddagger}_{25}$) for both the forward and reverse reactions to be on the order of 20–21 kcal/mol. These data may be compared to the energetics of ring opening of **23** to **24** ($\Delta G^{\ddagger}_{25}$ = 23.2 kcal/mol).[6a] Vogel[31] et al. have determined the activation parameters for ring opening of the parent bicyclooctatriene **25** to be E_a = 18.7 kcal/mol and A = 9.1 × 10^{11} s^{-1} from rate constants measured at 0 and 20 °C. The corresponding values for **13** (22.2; 2.3 × 10^{14}) and **14** (23.7; 1.3 × 10^{14}) are appropriately elevated as a consequence of steric interactions among the peripheral substituents.



Since the rates interconversion of **5** and **6** are considerably slower than the respective valence isomerizations, the stage was set for determination of the racemization behavior of (−)-**5**. As detailed previously elsewhere,[4f] the rates at which optical activity is lost is given by the expression

$$-\ln \alpha = 2(2k_2 + k_1)t - \ln \alpha_0$$

The factor of 2 is obligatory because production of (+)-**5** only results in loss of one molecule undergoing dynamic change but negates the rotatory power of a second. Also, **6** is generated twice as rapidly as (+)-**5** (Scheme II).

Table III. Exemplary Data for Racemization of (−)-5 (120 ± 0.2 °C)

time, s	α_{436}, deg	ln α_{436}
0	−0.097	−2.33
900	−0.076	−2.58
1800	−0.064	−2.75
2700	−0.053	−2.94
3900	−0.039	−3.24
5800	−0.028	−3.58
8200	−0.017	−4.07
11800	−0.010	−4.61

slope = 1.947 × 10^{-4}
y intercept = −0.0926
r = 0.966

Acquisition of Kinetic Data for RI and BS. The racemization rates were determined by heating degassed

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[31] Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 442.

Table IV. Rate Data for Bond Shifting in 5 and 6 and Activation Parameters for k_2 and k_{-2}

temp, K	slope ($\times 10^5$)	intercept	corr coeff	K_{eq}	k_2	k_{-2}
394.0[a]	2.1	−0.055	0.997	1.05	4.9×10^{-6}	5.1×10^{-6}
395.8[b]	2.9	−0.025	0.98	0.91	7.9×10^{-6}	7.1×10^{-6}
	2.8	−0.050	0.98	0.96	7.1×10^{-6}	6.0×10^{-6}
402.4[a]	7.6	−0.171	0.996	0.99	1.9×10^{-5}	1.9×10^{-5}
406.5[b]	8.4	0.064	0.93	1.0	2.1×10^{-5}	2.1×10^{-5}
	8.7	−0.17	0.95	1.0	2.2×10^{-5}	2.1×10^{-5}
414.7[b]	23	−0.19	0.96	0.98	6.1×10^{-5}	5.9×10^{-5}
	18	−0.008	0.97	0.97	4.6×10^{-5}	4.4×10^{-5}

Arrhenius Plots

$5 \xrightarrow{k_2} 6$	$6 \xrightarrow{k_{-2}} 5$
slope = $-1.75 \times 10^4 = E_a/R$	slope = $-1.78 \times 10^4 = E_a/R$
int = 32.4 = $\ln A$	int = 33.1 = $\ln A$
$r = -0.986$	$r = -0.986$
$E_a = (34.8 \pm 2.4)$ kcal/mol	$E_a = (35.4 \pm 2.4)$ kcal/mol
$\ln A = (32.4 \pm 3.0)$, $A = 1.2 \times 10^{14}\ \mathrm{s}^{-1}$	$\ln A\ (33.1 \pm 3.0)$, $A = 2.4 \times 10^{14}\ \mathrm{s}^{-1}$
$\Delta H^{\ddagger}_{25} = (32.4 \pm 2.4)$ kcal/mol	$\Delta H^{\ddagger}_{25} = (34.8 \pm 2.4)$ kcal/mol
$\Delta S^{\ddagger}_{25} = (3.9 \pm 5.9)$ eu	$\Delta S^{\ddagger}_{25} = (5.2 \pm 6.0)$ eu
$\Delta G^{\ddagger}_{25} = (33.1 \pm 2.5)$ kcal/mol	$\Delta G^{\ddagger}_{25} = (33.3 \pm 2.1)$ kcal/mol

[a] Experiments starting with 5. [b] Experiments starting with 6.

purified diglyme solutions of (−)-**5** at 100, 110, and 120 °C. Plots of $-\ln \alpha$ (Hg_{436} line) vs. time gave straight lines whose slopes were equal to $2(2k_2 + k_1)$. A sample data set is provided in Table III.

In order to extract the values for k_1, the rate constants for RI, from this composite kinetic term, the rate constants for BS were determined in the same temperature range. For this purpose, degassed diglyme-d_{14} solutions of **6** $\rightleftarrows$ **13** or **5** $\rightleftarrows$ **14** and dioxane (internal standard) were sealed in NMR tubes which were heated in a constant temperature bath and individually cooled to −78 °C at appropriate time intervals. The methyl regions of the expanded scale 90-MHz ^{1}H NMR spectra of these samples were integrated planimetrically with respect to the internal standard.[4,6] Such studies, which were made possible by the distinctive chemical shifts of the two isomers,[27] provided for the direct measurement of k_2 and k_{-2} and therefore activation parameters for BS (Table IV). The finalized rate data for ring inversion, together with activation parameters, are collected in Table V.

Discussion

Effects of Phenyl Substitution on Valence Isomerization. The peripheral phenyl substituents in **5** and **6** exert an effect on cyclooctatetraene valence isomerization which is somewhat more accentuated than that previously encountered in purely methylated derivatives. ^{1}H NMR studies on **27a–c** have, for example, provided indication of essentially homogeneous monocyclic features at room temperature within the limits of instrument detectability.[4] In contrast, **6** is only 54% monocyclic under comparable conditions. Similarly, whereas the medium-ring forms of **28a** and **28b** have both been shown spectrosopically to enjoy a thermodynamic advantage of approximately 3:1 over their bicyclic forms,[4] the equilibrium concentration gradient of **5** at room temperature is only 45%.

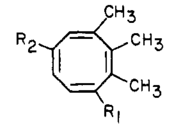
Table V. Rate Data and Activation Parameters for Ring Inversion (k_1) in 5

temp, K	racemization slope, $2(2k_2 + k_1)$	k_2, s^{-1} [a]	k_1, s^{-1}
393.3	1.9×10^{-4} 2.0×10^{-4}	5.4×10^{-6}	8.4×10^{-5} 8.9×10^{-5}
383.3	8.7×10^{-5} 7.7×10^{-5}	1.7×10^{-6}	4.0×10^{-5} 3.5×10^{-5}
373.3	2.9×10^{-5} 2.9×10^{-5}	5.0×10^{-7}	1.3×10^{-5} 1.3×10^{-5}

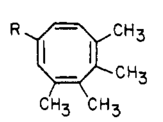
Arrhenius Plot ($\ln k_1$ vs. $1/T$)

slope = $-1.39 \times 10^4 = E_a/R$	$\ln A = (26.1 \pm 1.4)$, $A = 2.1 \times 10^{11}\ \mathrm{s}^{-1}$
int = 26.1 = $\ln A$	$\Delta H^{\ddagger}_{25} = (27.1 \pm 1.0)$ kcal/mol
$r = -0.997$	$\Delta S^{\ddagger}_{25} = -(8.7 \pm 2.7)$ eu
$E_a = (27.7 \pm 1.0)$ kcal/mol	$\Delta G^{\ddagger}_{25} = (29.7 \pm 1.2)$ kcal/mol

[a] Calculated from the bond shifting data.

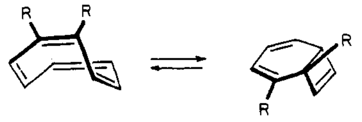


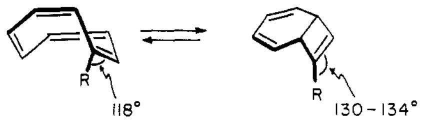
27a, $R_1 = R_2 = H$
b, $R_1 = CH_3$, $R_2 = H$
c, $R_1 = R_2 = CH_3$



28a, R = H
b, R = CH_3

Since the bicyclo[4.2.0]octatriene ring system is ~8.5 kcal/mol more strained than that of cyclooctatetraene,[6b] these data can be taken as an indication that nonbonded steric and pπ conjugative interactions in **5** and **6** can be better accommodated within **14** and **13**, respectively. Two factors could be responsible for this phenomenon. In the first, electrocyclization involving a disubstituted ring double bond serves to project the two external R groups, held originally in-plane, into widely divergent directions as illustrated. Substantial release of steric congestion should accompany ring closure in these circumstances. Secondly, an R group located on the cyclobutene double bond must be sterically less compressed vis-a-vis its neighboring substituent as compared to its status in the monocyclic tautomer because of structurally enforced widening of the external bond to roughly 130–134°[32] from 118°.[33]





The energetics operative within **6** $\rightleftarrows$ **13** and **5** $\rightleftarrows$ **14** can be understood in these terms if the phenyl rings in the

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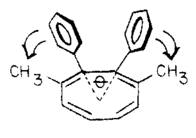
(32) Although no bicyclo[4.2.0]octatriene has been subjected to X-ray analysis, several prototypes have been examined: (a) Benedetti, T.; Ciajolo, M. R.; Declerq, J. P.; Germain, G. *Acta Crystallogr., Sect. B* **1974**, *30*, 2873. (b) Lemley, J. T.; Stezowski, J. J.; Hughes, R. E. *Ibid.* **1976**, *432*, 1212. (c) Franck, R. W.; Gruska, R.; White, J. G. *Tetrahedron Lett.* **1977**, 509.

(33) (a) Bordner, J.; Parker, R. G.; Stanford, R. H. *Acta. Crystallogr., Sect. B* **1972**, *28*, 1069. (b) Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724. (c) Bastiansen, O.; Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1957**, *27*, 1311. (d) Karle, I. L. *Ibid.* **1952**, *20*, 65.

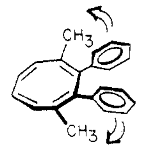
monocyclic forms are essentially perpendicular to the [8]annulene core. Electrocyclization within **6** to give **13** serves to splay the bonds to the two phenyl rings and allow for enhanced levels of conjugative overlap between these aryl substituents and adjacent double bond (partial *cis*-1,2-diphenylethylene character). The equilibrium might be somewhat more heavily shifted in the direction of **13** were it not for the presence of methyl groups at both angular sites. Although these alkyl substituents are also splayed in outwardly directions, some steric interaction is unavoidable.

The situation which leads to a dominance of **14** at room temperature is somewhat more dramatic. Whereas both phenyl groups in cyclooctatetraene **5** can *formally* enter into styrene delocalization, the angular phenyl in **14** cannot. Yet **14** is favored, presumably because of the sterically enforced out-of-plane geometry of the aryl substituents. The semblance of styrene character which is thought to be present in the bicyclooctatriene form, coupled with relief of nonbonded steric interactions, appears adequate to shift the equilibrium slightly toward **14**.

Peripheral Strain and the Ring Inversion Barrier. Molecular models suggest that the generally accepted geometry for RI transition states[4,6,34] will, in the case of **5**, bring the phenyl rings face-to-face as in **7**. Even in this conformation, the aryl groups appear to experience crowding adequately severe to impose a high barrier to rotation of any magnitude. In-plane splaying involving bending of the phenyl–COT σ bonds as in **29** cannot occur appreciably because of the buttressing effects of the flanking methyl groups. Therefore, a widening of angle θ by this mechanism cannot materialize without a concomitant increase in crowding between phenyl and methyl substituents. Out-of-plane splaying as in **30** would involve displacement of the phenyl rings (and to a lesser extent the COT ring atoms C2 and C3) to opposite sides of the plane defined by the eight-membered ring. This description is equivalent to the assumption that the aryl groups do not pass simultaneously through the plane defined by the [8]annulene core. Additionally, there exists no reason to discount the possibility that the COT nucleus can effectively absorb a portion of the overall strain energy and efficiently distribute it throughout its framework by suitable angle bending, bond stretching, and compression (but short of π-electron delocalization), and in- and out-of-plane nuclear displacements.



29



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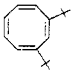
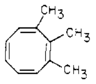
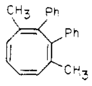
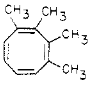
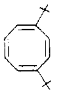
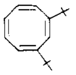
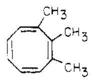
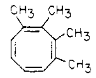
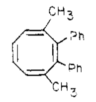
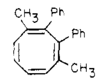
The facts are that the energy of activation (E_a) for ring inversion in **5** (27.6 kcal/mol) is appropriately higher than that determined for 1,2,3-trimethylcyclooctatetrane (23.0 kcal/mol) but still appreciably lower than that of 1,2,3,4-tetramethylcyclooctatetraene (29.1 kcal/mol; Table VI). This ordering, which places the attainment of **7** below **3** in energy costs, is opposite to that encountered with bond shifting (see below). It would appear, therefore, that the perturbation introduced by extensive peripheral steric crowding in a planar alternate cyclooctatetraene is spread throughout the [8]annulene framework. The lesser energy demands for **7** relative to **3** may be understood in terms of greater ring buckling in the first instance. Of course, the relative distribution of strain between the various out-of-plane modes will depend upon numerous factors determined by the nature and size of the substituents, as well by intraannular angle deformation forces.

Table VI. Ring Inversion Barriers for Sterically Congested Cyclooctatetraenes

COT	E_a, kcal/mol	ln A	$\Delta H^{\ddagger}_{25}$, kcal/mol	$\Delta S^{\ddagger}_{25}$, eu	$\Delta G^{\ddagger}_{25}$, kcal/mol	ref
	19.9	26.7	19.3	−7.5	21.6	6a
	23.0	26.6	22.4	−7.7	24.7	4e
	27.7	26.1	27.1	−8.7	29.7	present work
	29.1	24.9[a]	28.5	−11.0[a]	31.8	4f

[a] The original report lacked a minus sign for the $\Delta S^{\ddagger}$ value and had a typographical error in the ln A value.

Table VII. Bond Shifting Barriers for Sterically Congested Cyclooctatetraenes

COT	E_a, kcal/mol	ln A	$\Delta H^{\ddagger}_{25}$, kcal/mol	$\Delta S^{\ddagger}_{25}$, eu	$\Delta G^{\ddagger}_{25}$, kcal/mol	ref
			14.8	−26.3	22.6	7b
	23.3	29.0	22.7	−2.9	23.6	6a
	23.5	24.4	22.9	−12	26.5	4e
	28.7	24.4	28.1	−13.3	32.0	4f
	35.4	33.1	33.3	+5.2	33.3	present work
	34.8	32.4	32.4	+3.9	33.1	present work

Analysis of π Bond Shifting Energetics. The conclusion reached above tacitly assumes that a phenyl group located in the bisector plane of a flattened polyunsaturated eight-membered ring has greater steric requirements than

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(34) (a) Anet, F. A. L. *J. Am. Chem. Soc.* **1962**, *84*, 671. Anet, F. A. L.; Brown, A. J. R.; Lin, Y. S. *Ibid.* **1964**, *86*, 3576. Anet, F. A. L.; Bock, L. A. *Ibid.* **1968**, *90*, 7130. (b) Oth, J. F. M.; Merenyi, R.; Martini, Th., Schröder, G. *Tetrahedron Lett.* **1966**, 3087. Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573. (c) Gwynn, D. E.; Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.*, **1965**, *87*, 2862. (d) White, E. H.; Stern, R. L.; Lobl, T. J.; Smallcombe, S. H.; Maskill, H.; Friend, E. W., Jr. *Ibid.* **1976**, *98*, 3247.

a comparably situated methyl group during ring inversion. Suitable energetic adjustments might well result in distortion of the nondelocalized COT ring when the phenyls are in place. During the course of π bond shifting, the involvement of a delocalized medium-ring structure, viz. **9**, is inferred. Arrival at a planar structure with equal bond lengths as in **9** serves to restrict those conformational degrees of freedom previously available to the medium ring in its bond alternate counterpart **7** where cyclic conjugation is not at issue. A possible reason why **9** is more difficult to attain than **4** (Table VII) is understandable in terms of the enhanced in-plane congestion of the four peripheral substituents unavoidably caused by the greater need for planarity within the delocalized [8]annulene. The difference of approximately 6 kcal/mol in the E_a's for BS and RI is due in part to heightened compressional influences and in part to the energy required to drive the delocalization. Since an unfavorable resonance energy of 2–4 kcal/mol is generally seen,[5,29] the phenyl groups in **9** appear to be exerting relatively normal steric perturbations.

Although an interesting topogical distinction between **7** and **9** appears to exist, our analysis has been rendered somewhat complicated by the presence of two phenyl groups. Further refinement of the questions raised by the present work demand that the dynamic behavior of 1,3-dimethyl-2-phenyl-, 1,2-dimethyl-3-phenyl-, and 1,8-dimethyl-2-phenylcyclooctatetraene be quantitatively assessed. Such studies have been initiated.

Experimental Section

Proton magnetic resonance spectra were obtained with Varian EM-390 and Bruker HX 90 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***exo*- and *endo*-1,6-Dimethyl-7,8-diphenyltricyclo-[4.2.1.0^{2,5}]nona-3,7-dien-9-one (10 and 11).** The mixture of bridged ketones was obtained in 91% yield by dechlorination of the corresponding dichlorides according to Warrener et al.[24b]

Photolysis of 10 and 11. The ketone sample (4.4 g, 1.4 mmol) was dissolved in acetone (180 mL) and placed in two quartz tubes. These tubes were irradiated at 2537 Å in a Rayonet reactor. The irradiation was continued until the ratio of **12** to **10** and **11** was approximately 1:2. Usually, 3 h was required. The solvent was evaporated and half of the resulting oil was dissolved in a minimum amount of toluene and applied to a silica gel (60 g) column. Elution with petroleum ether furnished 1.5 g (38%) of bicyclic triene **12** as a pale-yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.4–6.5 (m, 10 H), 6.10 (s, 2 H), 3.50 (s, 2 H), 1.55 (s, 6 H).

Heating of **12** to 60–80 °C on a steam bath resulted in isomerization to a mixture of **6** and **13** as previously observed by Warrener.[25]

Generation of Mixtures of 5 and 6. The bicyclic triene **12** (685 mg) in diglyme (15 mL) was heated to 120–130 °C under nitrogen for 20 h. ^{1}H NMR analysis at this stage indicated the total disappearance of starting material and formation of **6** ⇄ **13** and **5** ⇄ **14**. The spectrum conformed nicely to that provided earlier by Warrener.[25,27]

When the reaction mixture was cooled to room temperature, a 10% molar excess of *N*-methyltriazolinedione was added and the solution was stirred for 90 min. After removal of the diglyme by vacuum distillation, the crude mixture (1.3 g) was dissolved in chloroform (10 mL) and divided into two portions. Separation was achieved on a Waters Prep 500 instrument using 30% ethyl acetate in petroleum ether as eluant. There was obtained 272 mg (29%) of **15** and 230 mg (25%) of **16** in a total yield of 55% from **10**. Both adducts were recrystallized from ethyl acetate.

For **15**: mp 219–220 °C (lit.[25] mp 220 °C); ^{1}H NMR ($CDCl_3$) δ 7.32 (s, 10 H), 6.22 (t, J = Hz, 2 H), 4.85 (t, J = 4 Hz, 2 H), 3.03 (s, 3 H), 1.55 (s, 6 H).

Anal. Calcd for $C_{25}H_{23}N_3O_2$: C, 75.55; H, 5.82. Found: C, 75.24; H, 5.81.

For **16**: mp 235–236.5 °C (lit.[25] mp 236 °C); ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (m, 10 H), 6.3 (m, 2 H), 5.2 (m, 1 H), 3.27 (br d, 1 H), 3.03 (s, 3 H), 1.80 (s, 3 H), 1.70 (s, 3 H).

Regeneration of 5 ⇄ 14 by Hydrolysis–Oxidation of 16. An isopropyl alcohol (10 mL) solution of **16** (104 mg, 0.26 mmol) and sodium hydroxide (110 mg, 2.7 mmol) was heated at reflux under nitrogen for 3.5 h, cooled to 0 °C, made acidic (pH ~1) by dropwise addition of 3 N hydrochloric acid, and finally made basic (pH ~8) with 3 N ammonium hydroxide solution. The reaction mixture was warmed to room temperature and *n*-pentane (5 mL) was added. Freshly prepared Attenburrow manganese dioxide (234 mg, 2.7 mmol) was added and the solution was stirred for 75 min and filtered. The residue was washed with pentane, water (20 mL) was added, and the layers were separated then the mixture was shaken. The aqueous phase was extracted with additional pentane (2 × 15 mL) and the combined organic solution was washed with water (2 × 15 mL) and brine (15 mL), dried, and concentrated. The resulting yellow oil (86 mg) was dissolved in a minimum amount of benzene, applied to a Florisil column (3 g), and eluted with pentane. Further purification by preparative layer chromatography (silica, petroleum ether) gave the hydrocarbon as a very pale yellowish solid (27 mg, 35%): ^{1}H NMR ($CDCl_3$) δ 7.3–6.7 (m), 6.4–5.5 (m), 2.91 (m), 2.07 (d, $J \sim$ 2 Hz), 1.66 (br s), 1.59 (s).[27]

Formation and Separation of Urazoles 18 and 19. To a solution of **5** ⇄ **14** (90.4 mg, 0.33 mmol) in ethyl acetate (5 mL) was added a solution of (–)-**17** (103 mg, 0.43 mmol) in ethyl acetate (20 mL) at room temperature. Instantaneous fading of color was noted. After being stirred for 10 h, the solvent was evaporated and the resulting pink oil was filtered through silica gel to remove unreacted (–)-**17**. Following this, the separation of **18** and **19** was effected by preparative layer chromatography on silica gel (elution with petroleum ether–ether, 10:1, 14 developments). The higher R_f component, subsequently identified as (+)-**18** was obtained as colorless crystals, mp 201–203 °C (from petroleum ether–ether, 61.9 mg), having the following polarimetric properties: $[\alpha]^{20}{}_D$ +12.14°, $[\alpha]^{20}{}_{578}$ +12.9°, $[\alpha]^{20}{}_{546}$ +15.5°, $[\alpha]^{20}{}_{436}$ +36.64° (*c* 34.5, C_2H_5OH); ^{1}H NMR ($CDCl_3$) δ 7.53–7.0 (m, 10 H), 6.46–5.95 (m, 2 H), 5.27–5.0 (m, 1 H), 4.5–4.0 (m, 1 H), 3.2 (br d, J = 4 Hz, 1 H), 2.66–1.2 (series of m, 7 H), 1.80 (s, 3 H), 1.72 (s, 3 H), 0.98 (s, 3 H), 0.90 (s, 3 H), 0.81 (s, 3 H); mass spectrum m/e calcd for $C_{34}H_{37}N_3O_2$, 519.2886, obsd 519.2896.

The lower R_f component was obtained as colorless crystals (42.5 mg) from petroleum ether–ether: mp 215–216 °C; $[\alpha]^{20}{}_D$ –38.5°, $[\alpha]^{20}{}_{578}$ –40.8°, $[\alpha]^{20}{}_{546}$ –47.8°, $[\alpha]^{20}{}_{436}$ –97.2° (*c* 6.6, C_2H_5OH); ^{1}H NMR was indistinguishable from that of **18** at 90 MHz.

Anal. Calcd for $C_{34}H_{37}N_3O_2$: C, 78.58; H, 7.18. Found: C, 78.42; H, 7.23.

X-ray Crystal Structure Analysis of (–)-19. The crystals of **19** were orthorhombic, space group $P2_12_12_1$, with a = 12.814 (8) A, b = 14.516 (6) A, c = 15.337 (6) Å, and d_{calcd} = 1.209 g cm^{-3} for Z = 4 ($C_{34}H_{37}N_3O_2$, M_r 519.69). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). A crystal measuring approximately 0.25 × 0.4 × 0.6 mm was used for data collection. A total of 2185 reflections were measured for $\theta < 57°$, of which 2035 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[35] and was refined by the full-matrix least-squares method. One reflection which was strongly affected by extinction was excluded from the final refinement and final difference map. In the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are R = 0.041 and R_w = 0.051 for the remaining 2034 observed reflections. The final difference map has no peaks

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[35] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, *27*, 368.

greater than ±0.2 e Å^{-3}. The numerical data associated with this determination are supplied as supplementary material.

Hydrolysis–Oxidation of (−)-19. A 102-mg (1.19 mmol) sample of (−)-19, $[\alpha]^{20}_D$ −38.5°, dissolved in 20 mL of isopropyl alcohol was heated to reflux with sodium hydroxide (425 mg) under a nitrogen atmosphere for 24 h. The cooled reaction mixture was made acidic by addition of 3 N hydrochloric acid and then made basic with 3 N ammonium hydroxide solution. The product was extracted into ether (3 × 50 mL), and the combined ether layers were washed with water and brine prior to drying. The filtered solution was treated with activated manganese dioxide (500 mg) under nitrogen and the mixture was stirred at room temperature for 40 min. The excess MnO_2 was filtered off and the filtrate was concentrated in the absence of heat to leave a brown oil. This material was purified by low temperature (−35 to −40 °C) chromatography on Florisil (elution with petroleum ether) to give 20.5 mg (38%) of (−)-5 as a colorless oil: $[\alpha]^{20}_D$ −24.3° (*c* 10, ether).

Analogous treatment of (+)-18 (367 mg, 0.68 mmol), $[\alpha]^{20}_D$ + 23.2° (*c* 5.5, C_2H_5OH), afforded 99 mg of (+)-5, $[\alpha]^{20}_D$ +11.5° (*c* 49.5, ether).

Procedure for the Determination of the Rates of Racemization. Levorotatory 5 (79 mg) was dissolved in 3 mL of purified diglyme (freshly distilled from Na-K alloy) and the diglyme solution was divided into 23 glass tubes (sample volume 0.12–0.13 mL). Each tube was sealed under high vacuum after three freeze–thaw cycles. Analogously, a 99-mg sample of (+)-5, $[\alpha]^{20}_D$ +11.5° (*c* 49.5, ether), dissolved in 3 mL of purified diglyme was distributed among 26 tubes.

After the addition of a group of tubes to a constant temperature bath, a short equilibration period (ca. 5 min) was allowed to pass and a tube was removed as an accurate timer was started and quenched at −78 °C. Tubes were then removed and quenched at appropriate times. Each tube was opened, the solution was placed in a 0.1-dm polarimeter cell, and the rotation was recorded at 436 nm. Each rotation was plotted, using the previously described rate law, and the method of least squares was applied to evaluate the rate constants.

Procedure for the Determination of the Rates of Bond Shifting in 5 and 6. A small amount of 5 or 6 (ca. 30 mg) and dioxane (2–3 μL) were dissolved in diglyme-d_{14} in an NMR tube. Solutions were degassed by repeated freeze–thaw cycles (liquid nitrogen, three cycles) and sealed under high vacuum. The samples were heated in a constant temperature bath and a short equilibration period (about 2 min) was allowed for each measurement. As each tube was removed, it was cooled to −78 °C and its ^1H NMR spectrum (90 MHz) was recorded. The total amount of $C_{22}H_{20}$ isomers relative to dioxane did not change at 128.2 °C over a period of 32.5 h. The expanded scale methyl region was integrated, using a planimeter relative to the dioxane singlet. The data were plotted, using the previously described rate law, and the method of least squares was applied to evaluate the rate constants.

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Registry No. 5, 31462-32-5; (−)-5, 79980-69-1; (+)-5, 79980-70-4; 6, 79980-71-5; 10, 30450-25-0; 11, 64363-61-7; 12, 79918-56-2; 13, 79918-57-3; 14, 79918-58-4; 15, 31462-33-6; 16, 31462-35-8; (−)-17, 73462-83-6; (+)-18, 79918-59-5; (−)-19, 79980-72-6.

Supplementary Material Available: Tables of atomic coordinates with standard deviations, bond lengths, and bond angles together with their associated standard deviations (6 pages). Ordering information is given on any current masthead page.

Electronic Control of Stereoselectivity. 11. Long-Range Modulation of Stereoselection in Diels–Alder Cycloadditions of *N*-Methyltriazolinedione to Aryl-Substituted 9-Butadienylidenebenzonorbornenes[1]

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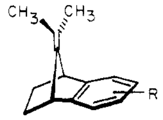
Three 9-butadienylidenebenzonorbornenes (**4a–c**) have been synthesized and their ability to enter into Diels–Alder reaction examined. Although these substances are unreactive to a host of dienophiles, tetracyanoethylene enters into [2 + 2] addition with **4b** and **4c**. However, these reactions do not allow for examination of the stereoselectivity question. When recourse was made to the more reactive *N*-methyltriazolinedione reagent, [4 + 2] adducts 9 and 10 were produced in the following syn/anti ratios: **4a**, 49:51; **4b**, 24:76; **4c**, 24:76. The chemical shifts of the *N*-methyl groups in the urazole segments of these adducts proved quite divergent and conducive to reliable structural assignment. The results are interpreted in terms of zwitterion intervention, with charge delocalization into the aromatic ring where this is feasible (the tetrafluoro example excluded). Because of this long-range homoaromatic stabilization, closure of the second C–N bond from the anti direction is kinetically favored.

The syn/anti stereoselection which operates when aryl-substituted 9-isopropylidenebenzonorbornenes (1) and related molecules engage in reaction with electrophiles has proven to be a convenient tool with which to assess relative electrophilicity.[3-7] For those weaker reagents which depend upon π-bond-induced polarization for their reactivity and which consequently engage in bridged ion formation



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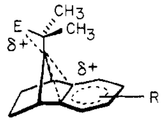

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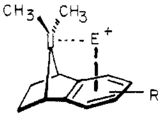

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