Bond Fixation in Annulenes. 11. Synthesis and Absolute Configuration of the Enantiomeric 1,3-Di-*tert*-butylcyclooctatetraenes. Quantitative Kinetic Assessment of the Effect of Nonvicinal *tert*-Butyl Groups on [8]Annulene Ring Inversion and Bond Shifting Barriers[1]

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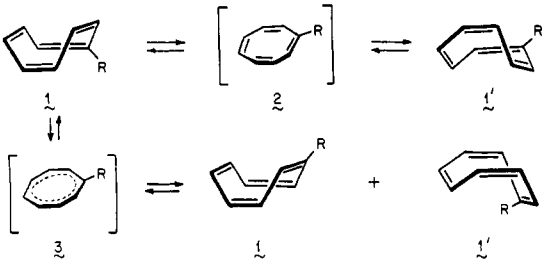
Abstract: On treatment with cyclobutadiene, 3,5-di-*tert*-butyl-*o*-benzoquinone was transformed into a Diels–Alder adduct (**10**), photolysis of which at ice-bath temperatures afforded 2,4-di-*tert*-butylbicyclo[4.2.0]octatriene (**12**). During warming to room temperature, this hydrocarbon underwent disrotatory ring opening to provide the cyclooctatetraene derivative (**7**). Cycloaddition of **7** and *endo*-bornyltriazolinedione (**15***) provided a diastereomeric pair of products which were separated by fractional crystallization. X-ray analysis of one of these isomers allowed assignment of absolute configuration to be made. Hydrolysis–oxidation gave the corresponding optically active cyclooctatetraene whose rates of racemization were determined. Since the slopes of the straight lines so obtained equal $2(k_{RI} + 2k_{BS})$, independent measurement of bond shifting rates was also undertaken. The requisite isotopically labeled COT was prepared analogously by means of cyclobutadiene-d_4. In addition to detailed information on the dynamic ring inversion and bond shifting processes, quantitative kinetic data on the bicyclooctatriene → COT valence isomerization was also retrieved. Not only were the consequences of positioning a pair of *tert*-butyl groups in a 1,3 relationship on an [8]annulene perimeter documented, but the basis for recognizing cyclooctatetraenes as weakly antiaromatic systems was further extended.

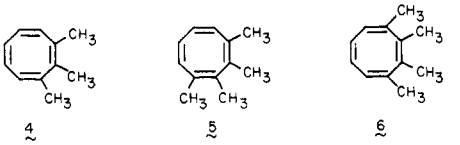
As a direct result of the position of cyclooctatetraene as the smallest nonplanar [4*n*]annulene, a complete understanding of the dynamic conformational behavior of this ring system has commanded considerable attention. Experiments reported several years ago established that ring inversions, i.e., reversible mechanical conversions of one tub conformation to another, involving monosubstituted derivatives such as **1** ⇄ **1′** required the surmounting of a 12.7–14.7 kcal/mol energy barrier.[5,6] This and additional available evidence are fully in agreement with Anet's original proposal[7] that planar-alternate transition states (**2**) are involved. Cyclooctatetraenes are also capable of bond shifting, a process usually[8] characterized by higher energy demands (>17 kcal/mol for **1**[5,9]). These isodynamical structural alterations are considered to be mediated by planar-delocalized transition states (**3**)[1,7] and have been intimately associated with the question of "antiaromatic" π-electron delocalization.

Theoreticians now agree that the dominant energy contributions in cyclooctatetraene have their origin in angular strain and nonbonded steric interactions.[6,10–12] In fact, Wirz, Allinger, and co-workers have concluded that "cyclooctatetraene puckers simply because the system is more (energetically) comfortable in the puckered form" and, more relevantly, that its "π system has a minimum of energy when it is planar, and puckering the system increases the π energy".[12] These effects seriously becloud those contributions which arise from cyclic conjugation as in **3**. The theoretical significance of the delocalization energy of **3** is not inconsequential, and some time ago we initiated a program to investigate this question in depth. Our methodology is dependent upon the ability to prepare an *optically active* cyclooctatetraene and to determine its rate of racemization. Since both bond shifting and ring inversion lead effectively to racemization (see Scheme I), independent experimental determination of one of these rate constants is necessary for complete quantitative definition of the kinetic parameters. The alternative assessment of k_{BS} by proper deuterium substitution of the substrate polyolefin, in tandem with variable-temperature ^{1}H NMR spectroscopy, has proven most often workable. In this way, direct comparison of the free energies of activation for ring inversion (RI) and bond shifting (BS) becomes possible.

Scheme I



The optically active cyclooctatetraenes which have been prepared to date have had three or four substituents bonded *contiguously* as in **4** and **5**.[8,13–15] This substitution plan generates added



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(8) The only documented example where k_{RI} is not greater than k_{BS} is the 1,2,3,4-tetramethyl derivative where $k_{RI} = k_{BS}$ within experimental error: (a) Gardlik, J. M.; Paquette, L. A.; Gleiter, F. *J. Am. Chem. Soc.* **1979**, *101*, 1617. (b) Paquette, L. A.; Gardlik, J. M.; Johnson, L. K.; McCullough, K. J. *Ibid.* **1980**, *102*, 5026.
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steric encumbrances on the periphery of the ring system, thereby inhibiting the attainment of planar-alternate or planar-delocalized transition states and actually making possible the isolation of shelf-stable bond shift isomer pairs, e.g., **5** and **6**.[8,14] The magnitude of $\Delta\Delta G^{\ddagger}$ which separates k_{BS} and k_{RI} in any cyclooctatetraene is determined by subtraction of two small and relatively accurate numbers and is consequently highly reliable from the experimental standpoint. However, it is necessary to recognize that such $\Delta\Delta G^{\ddagger}$'s can only be approximations of the [8]annulene delocalization energy since they necessarily encompass those differences in energetic and steric demands (including buttressing effects) that distinguish **2** from **3**.[1] Thus, progression through a series bordered by 1,2-Me_2COT and 1,2,3,4-Me_4COT shows the differences in $\Delta\Delta G^{\ddagger}$ to decrease as the level of external steric congestion increases.[1]

Because the minimization of peripheral steric constraints need maximize the contribution of electronic factors to $\Delta\Delta G^{\ddagger}$, we have turned our attention to 1,3-di-*tert*-butylcyclooctatetraene (**7**), a noncontiguously substituted [8]annulene regarded as potentially borderline in its ability to support optical activity. The weight of evidence, minimal as it presently is, suggests that should **7** be resolvable, its rate of racemization would be rapid. This conclusion is predicated in particular upon the compressional boundary which materializes when a hydrogen atom is forced to be coplanar with two flanking *tert*-butyl groups. To our knowledge, the only experiments designed to permit recognition of the steric congestion surrounding such a substitution plan have involved 2,6-di-*tert*-butylpyridine (**8**). As subjects of detailed physical organic studies, 1,3,5-tri-*tert*-butylbenzene[16] and *m*-di-*tert*-butylbenzene[17] have been shown to be substantively less strained than their 1,2-disubstituted isomers, but information on their intrinsic strain is unavailable. Brown and Kanner have shown that a small linear increase in base strength is exhibited by the series pyridine (pK_a = 4.38), 2-isopropylpyridine (4.82), and the 2,6-diisopropyl derivative (5.34).[18] 2-*tert*-Butylpyridine (4.68) follows the same pattern, but introduction of a second *tert*-butyl group as in **8** causes a sharp p*K*a *decrease* to 3.58 (the projected value is 4.98, a discrepancy of 1.4 units). Although **8** does react with hydrogen chloride, a simple 1:1 hydrochloride salt does not result.[18] Furthermore, the conversion of **8** to its *N*-methylpyridinium salt can be satisfactorily accomplished only with methyl fluorosulfonate under high pressure.[19]

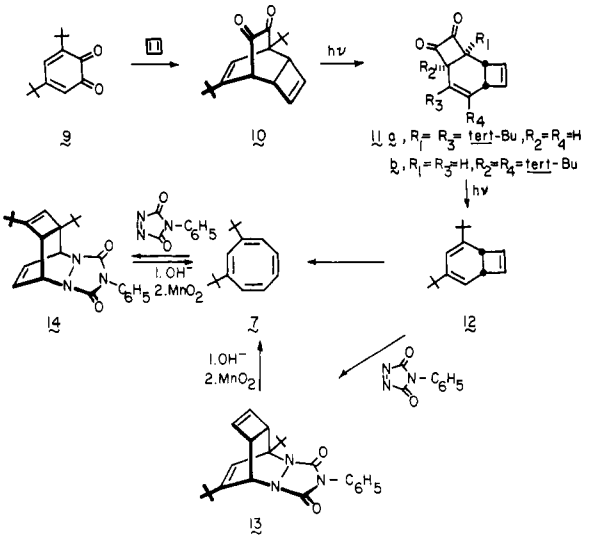
The effect of the neighboring *tert*-butyl groups on the incipient $=N^{+}(-)$—H bond in the potonated counterpart of **8** is clearly to promote unusual chemical behavior.[20] In the planar forms of 1,3-di-*tert*-butylcyclooctatetraene (**7**) corresponding to **2** and

7 **8**

3, the internal angles are larger than those in **8**, and consequently the compressional energies between the pair of *tert*-butyl groups and flanking hydrogens can be expected to be somewhat more accentuated. With the present work, there is provided some indication of the energetics of such interactions in the absence of appreciable solvation demands,[20] as well as added insight into the question of 8π-electron delocalization.

Results

Synthesis and Chemical Behavior of Racemic 1,3-(t-Bu)$_2$COT.[21] Directed synthetic approaches to 1,3-disubstituted cyclooctatetraenes remain sorely lacking.[22,23] The only known example prior to this study was the 1,3-dimethyl derivative, available by pyrolysis of 1,3-dimethylsemibullvalene.[24] Because this approach appeared inadequately expedient for the desired *tert*-butyl substitution plan, a new route to **7** was developed. 3,5-Di-*tert*-butyl-*o*-benzoquinone (**9**), readily available by oxidation[25] of the



9 **10** **14** **7** **12** **13**

commerical catechol, was treated with cyclobutadiene as liberated from its $Fe(CO)_3$ complex.[26] The bright yellow crystalline α-diketone **10**, isolated in 51% of theory, exhibited ^{1}H NMR features in full agreement with the endo stereochemical assignment (see Experimental Section).

When dilute chloroform solutions of **10** were irradiated at 0–5 °C (iced water cooling) with 200- or 450-W Hanovia lamps, there was observed a gradual color change from yellow to reddish-pink, and finally to colorless. Subsequent experiments conducted in Haifa by Professor Mordecai Rubin using benzene solutions of **10** established that irradiation at 436 nm leads to clean development of a new maximum at 514 nm. The product, which was stable for at least 1 h at room temperature, is assumed to be a mixture of the 1,2-cyclobutanedione isomers **11a** and **11b**.[27,28] Subsequent irradiation at 536 nm caused disappearance of the 514-nm band and formation of bicyclo[4.2.0]octatriene **12**. The structural assignment to **12** is in complete agreement with its spectroscopic features. The ^{1}H NMR spectrum ($CDCl_3$ solution) consists inter alia of a multiplet of area 2 at δ 6.1–5.9 due to the cyclobutenyl protons, a pseudo-singlet at δ 5.7 arising from H_6, a doublet (J = 3.5 Hz) at 5.85 for H_8, and overlapping multiplets in the 3.65–3.35 region attributable to the two bridgehead protons. Chemical evidence for the bicyclic formulation was obtained by reaction with *N*-phenyltriazolinedione at room temperature. The lone adduct produced (**13**) exhibits appropriate signals for a lone bridgehead proton (m, δ 5.28–5.12), three olefinic protons (m,

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(15) (a) Paquette, L. A.; Gardlik, J. M.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 7096. (b) Gardlik, J. M.; Johnson, L. K.; Paquette, L. A.; Solheim, B. A.; Springer, J. P.; Clardy, J. *Ibid.* **1979**, *101*, 1615. (c) Gardlik, J. M.; Paquette, L. A. *Tetrahedron Lett.* **1979**, 3597. (d) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 5033.
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(26) (a) Paquette, L. A.; Leichter, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 5128. (b) Brener, L.; McKennis, J. S.; Pettit, R. *Org. Synth.* **1976**, *55*, 43.
(27) Rubin, M. R.; Weiner, M.; Scharf, H.-D. *J. Am. Chem. Soc.* **1976**, *98*, 5699.
(28) Warrener, R. N.; Russell, R. A.; Lee, T. S. *Tetrahedron Lett.* **1977**, 49.

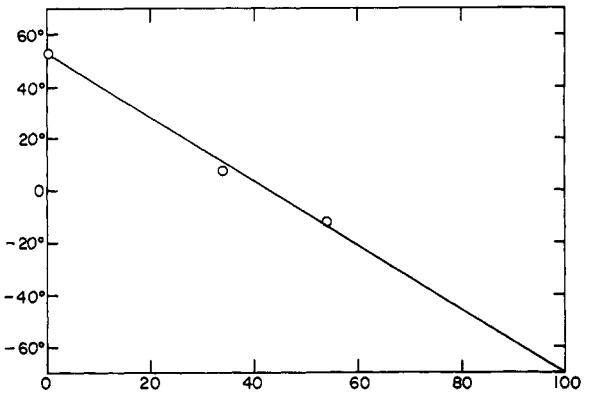
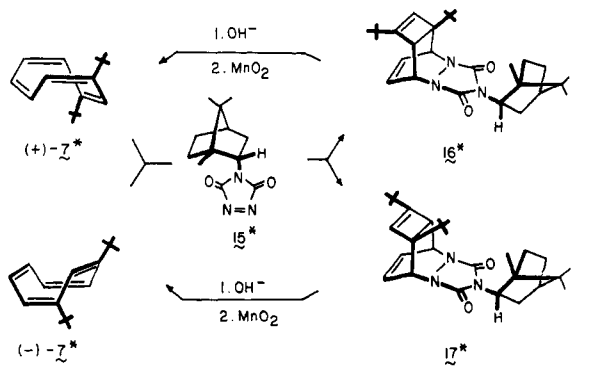


Figure 1. Plot of specific rotation, $[\alpha]_D$, vs. percent of the levorotatory diastereoisomer present in adducts **16*** and **17***.

6.0–5.85), and two methine protons in a four-membered ring (m, 3.55–3.27). Additionally, storage of **12** at room temperature for 1 h results in complete conversion to the desired cyclooctatetraene, a colorless liquid. The conversion of **10** to **7** proceeds in 84% yield. When heated with *N*-phenyltriazolinedione in ethyl acetate solution, **7** is converted exclusively to urazole **14** where the bulky *tert*-butyl substituents are now positioned on the cyclobutene ring. Particularly characteristic of **14** are its three magnetically distinctive olefinic protons which appear at δ 6.3 (ddd, J = 7, 6.5, and 2 Hz), 5.94 (ddd, J = 6.5, 6.5, and 1.5 Hz), and 5.60 (d, J = 2 Hz), and its pair of bridgehead protons (m, 5.2–4.82). Expectedly,[29] kinetically controlled Diels–Alder addition to **7** proceeds preferably via that valence tautomer which is denuded of *tert*-butyl groups on the conjugated diene unit. Submission of either **13** or **14** to sequential alkaline hydrolysis and manganese dioxide oxidation[30] regenerated **7**.

When viewed in its ground-state "tub" geometry, **7** is seen to possess two chemically different *tert*-butyl groups and to belong to the C_1 point group. In agreement with these features, its ^1H NMR spectrum displays a series of multiplets due to six olefinic protons and a pair of singlets at δ 1.08 and 1.05 (9 H each). Also, the ^{13}C NMR spectrum consists of 12 lines. These data reveal that **7** is not experiencing very rapid π-bond shifting under the conditions of spectral measurement.

Direct Resolution of 1,3-(t-Bu)$_2$COT. Absolute Configurational Assignments. The separation of **7** into its enantiomers was accomplished by heating the racemic cyclooctatetraene with (−)-*endo*-bornyl-1,2,4-triazoline-3,5-dione (**15***).[8b,15] The oily mixture



of diastereomeric urazoles **16*** and **17*** was crystallized from hexane. By fractional crystallization of the resulting solid from petroleum ether and petroleum ether–ether solvent systems, it proved possible to obtain pure samples of both adducts. To gain information on diastereomeric purity, various samples were subjected to lanthanide-induced shifting with tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III). Since

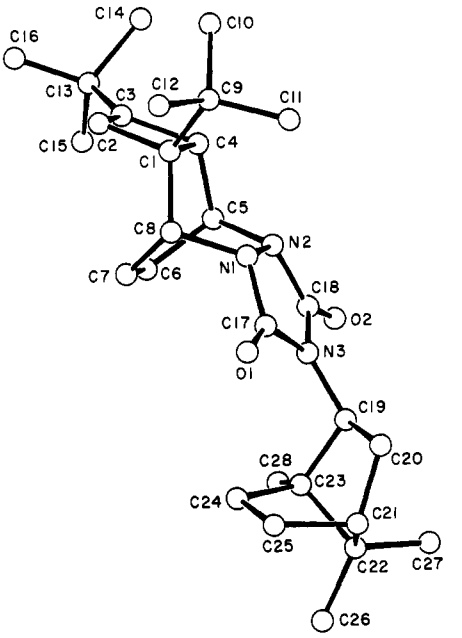


Figure 2. A computer-generated perspective drawing of **17***. Hydrogen atoms are omitted for clarity and the absolute configuration is discussed in the text.

diastereomers and not enantiomers are involved, a chiral shift is not required in principle. However, advantage was taken of the fact that the presence of 0.11 mol equiv of this chiral shift reagent caused the pair of *tert*-butyl singlets of the levorotatory isomer to appear at δ 1.1 and 1.0 (in $CDCl_3$), distinctly separated from the two signals characteristic of the dextrorotatory isomer (δ 1.3 and 1.05). Integration of these peaks made it possible to obtain a linear correlation of diastereomeric purity with specific rotation (Figure 1).

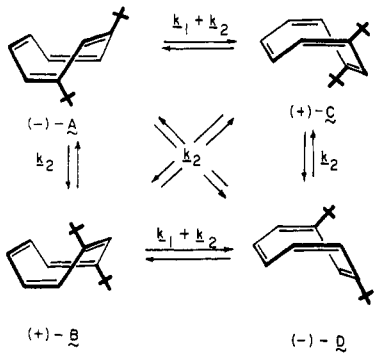
For the purpose of establishing the structural identity of the two diastereoisomers, a sample of **17***, $[\alpha]^{23}_D$ +56.6° (*c* 6.7, C_2H_5OH), was subjected to X-ray crystal structure analysis. In this instance, the well-known absolute configuration of the *endo*-bornylamine part structure[31] was to be utilized to achieve absolute configurational assignment to the remainder of the molecule in the usual fashion. A computer-generated perspective drawing of the final X-ray model of **17*** is given in Figure 2. In general, its molecular parameters were found to agree well with generally accepted values. These data may be found in the Supplementary Material. With this information in hand, it became possible to make absolute configurational assignments to enantiomeric 1,3-di-*tert*-butyl COT's with confidence.

The hydrolysis of pure (−)-**16*** was achieved most expediently by stirring with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature for 30–40 h under a nitrogen atmosphere. Following appropriate dilution with water and pH adjustment (see Experimental Section), oxidation was accomplished with 10 mol equiv of manganese dioxide in ether at −70 °C during 30–40 min. Subsequent chromatography of the organic phase on Florisil at −45 to −40 °C and flash evaporation of solvent at 0 °C gave (+)-**7***. Kinetic experiments to be described subsequently reflect the fact that considerable racemization of the [8]annulene had occurred during the requisite workup and handling. Comparable treatment of (+)-**17*** provided (−)-**7***.

Isodynamical Processes in 1,3-(t-Bu)$_2$COT. Racemization Kinetics. Ring inversion in (−)-A results in conversion to (+)-C at a rate defined herein as k_1, the magnitude of which relates equally to the reverse reaction and to the (+)-B ⇄ (−)-D change. When bond shifting occurs, it is assumed that adequate energy is available at the transition state to allow not only the conversion

(29) Paquette, L. A.; James, D. R.; Birnberg, G. H. *J. Am. Chem. Soc.* **1974**, *96*, 7454.
(30) James, D. R.; Birnberg, G. H.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 7465.
(31) (a) von Auwers, K. *Chem. Ber.* **1889**, *22*, 605. (b) Forster, M. O. *J. Chem. Soc.* **1898**, *73*, 386. (c) Hückel, W.; Rieckmann, P. *Justus Liebigs Ann. Chem.* **1959**, *625*, 1.

Scheme II



of (−)-A to (+)-B, but to (+)-C and (−)-D (simultaneous RI and BS) as well (see Scheme II). Stated differently, the attainment by an [8]annulene of an energy level demanded by **3** should allow return to any of the other three isodynamical structures as well as to itself. The rate constant for this process is termed k_2. As derived explicitly in earlier papers,[8b,15d] the overall loss of optical activity in (+)-**7*** or (−)-**7*** can be expressed by the equation

$$-d\alpha/dt = 2(k_1 + 2k_2)\alpha$$

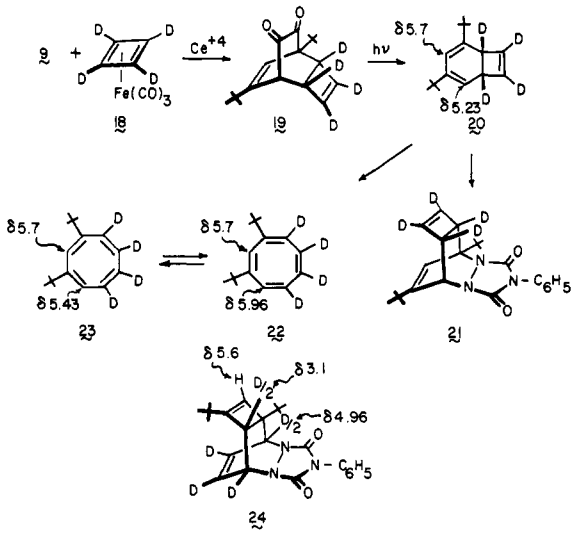
whose integration between the limits of $t = 0$ and $t = t$ yields the integrated rate law

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

The factor 2 arises as a consequence of the fact that formation of an enantiomer results not only in loss of the molecule experiencing the dynamic change, but also in cancellation of the rotatory power of a second.

The delicate racemization experiments were conducted on freshly prepared ethanol solutions of (+)-**7*** which were immediately placed in a 1-dm cell maintained at −3.0, 11.5, or 18.5 °C by means of a circulating constant-temperature bath. The rotations at 436 nm were recorded as a function of time, and plots of $-\ln \alpha$ vs. time afforded straight lines whose slopes are equal to $2(k_1 + 2k_2)$. The data compiled for duplicate runs at each temperature, together with the activation parameters, are summarized in Table I. In all instances, the racemization experiments were carried to completion (no further change in α after arrival at 0 °C), and the racemized 1,3-(t-Bu)$_2$COT was checked for purity by both thin layer chromatography and ^{1}H NMR analysis. No contamination from possible optically active (or other) byproducts was seen.

Preparation of the d_4 Derivative and Determination of Bond Shifting Rates. The next phase of the mechanistic problem, i.e., independent determination of k_2, was solved by identification of methodology for the exclusive preparation of deuterated bicyclooctatriene **20**. Since H–D exchange in cyclobutadieneiron tricarbonyl can be effected in CF_3COOD solution under an inert atmosphere,[32] the preparation of **19** could be readily accomplished. When photolyzed at 0 °C in chloroform solution, **19** was transformed uniquely into **20** whose deuterium substitution plan was confirmed by spectral analysis and conversion to urazole **21**. The ^{1}H NMR spectrum of **21** (in $CDCl_3$) showed only one weakly coupled olefinic proton (δ 5.92, d, J = 2 Hz) and a single bridgehead proton (5.2, d, J = 2 Hz). None of the absorptions associated with the cyclobutene ring in its protio counterpart **13** was in evidence.

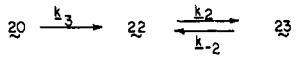


The pair of vinyl protons present in **20** appear as two relatively narrow multiplets centered at δ 5.7 and 5.23. Submission of **21** to hydrolysis–oxidation, with particular emphasis placed on a low-temperature workup, afforded a hydrocarbon mixture which exhibited four low-field signals of dramatically unequal intensity: δ 5.96 (w), 5.7 (s), 5.43 (w), and 4.23 (s). When this solution was allowed to stand at room temperature, the peak at δ 5.23 gradually decreased in relative area and ultimately disappeared altogether. Simultaneously, the intensities of the δ 5.96 and 5.43 signals were seen to increase, although at different rates. Throughout this period, the 5.7-ppm peak maintained its relative area of 1.

Addition of *N*-phenyltriazolinedione to the thermally equilibrated solution afforded an adduct identified as **24**. The structurally diagnostic ^{1}H NMR absorptions of this urazole appear at δ 5.6, 4.96, and 2.1 in a ratio of 2:1:1, respectively. This distribution (see formula) reveals that those species present after the establishment of equilibrium consist of an equimolar mixture of the bond shifted cyclooctatetraene isomers **22** and **23**.

Quite unexpectedly, our planned kinetic analysis was greatly facilitated by the finding that the somewhat isolated ring protons positioned *between* the *tert*-butyl groups in **20**, **22**, and **23** resonate at a common chemical shift (δ 5.7). As the ring opening of **20** progresses, a gradual diminution in the intensity of its second olefin proton (δ 5.23) is seen, with the most downfield peak (5.96) increasingly more rapidly in area than that at 5.43. On the assumption that **20** adheres to the strictures of orbital symmetry and experiences cyclohexadiene-controlled disrotatory electrocyclization,[1,8,13-15] **22** will necessarily be formed first and be the species responsible for the δ 5.96 absorption. The ensuing reversible bond shifting leading from **22** to **23** provides the ultimate means for total equilibration of the system.

Therefore, the overall kinetic situation with which we are dealing reduces to



Of the three rate constants, the determination of k_3 which is associated with the electrocyclic ring-opening step is quite straightforward. A distinction between the forward (k_2) and reverse (k_{-2}) bond shifting rate constants can be made only as a consequence of the placement of the four deuterium atoms on the [8]annulene ring. Therefore, k_2 and k_{-2} are interrelated by a deuterium isotope effect which is certain to be negligibly small in the present context. During the interconversion of **22** and **23**, the issue revolves around the degree of kinetic deceleration which may materialize when one of the *tert*-butyl groups passes by a neighboring C–H bond (relative to a somewhat shorter C–D bond) with which it is not already coplanar. For **22**, it is the proton which resonates at δ 5.96 which is in question, while for **23** a deuterium atom is involved. Any kinetic contributions from this phenomenon should be quite minor and we therefore set $k_2 = k_{-2}$.

For the acquisition of kinetic data, expanded scale ^{1}H NMR spectra were recorded at three temperatures on a Bruker HX-90 spectrometer fitted with a thermostated probe. To obtain the relative ratios of **20**:**22**:**23** as a function of time, the olefinic proton region was integrated, and the areas of the well-separated δ 5.23, 5.96, and 5.43 signals were internally calibrated against the δ 5.7

(32) (a) Barborak, J. C. Ph.D. Dissertation, University of Texas, 1968. (b) Paquette, L. A.; Malpass, J. R.; Krow, G. R. *J. Am. Chem. Soc.* **1970**, *92*, 1980.

Table VII. Summary of Kinetic Data and Activation Parameters

rate const	E_{act}, kcal/mol	$\Delta H^{\ddagger}$, (25 °C), kcal/mol	$\Delta S^{\ddagger}$, (25 °C), kcal/mol	$\Delta G^{\ddagger}$, (25 °C), kcal/mol	correlation coeff
k_{rac}	20.2	19.6	−5.1	21.1	−0.9907
k_1	19.9	19.3	−7.5	21.6	−0.9999
k_2	23.3	22.7	−2.9	23.6	−0.9988
k_3	28.4	27.8	15.4	23.2	−0.9966

peak whose relative intensity remained invariant at 1 H.

As concerns the present kinetic scheme, the mole fraction of **22**, α_{22}, as a function of time is given by

$$d\alpha_{22}/dt = k_3\alpha_{20} - k_2\alpha_{22} + k_2\alpha_{23} \quad (1)$$

$$= (k_3 - k_2)\alpha_{20} - 2k_2\alpha_{22} + k_2 \quad (2)$$

for $\alpha_{20} + \alpha_{22} + \alpha_{23} = 1$. Since the mole fraction of **20**, α_{20}, is independent of α_{22}, eq 2 may be rewritten as

$$d\alpha_{22}/dt + 2k_2\alpha_{22} = \alpha_{20(0)}(k_3 - k_2)e^{-k_3t} + k_2 \quad (3)$$

Equation 3 is a linear differential equation which may be solved by standard methods. With the initial mole fraction of **22** at $t = 0$ defined as $\alpha_{22(0)}$, the general solution is given by

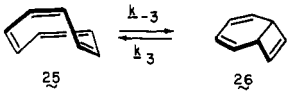
$$\alpha_{22} = \alpha_{20(0)}\frac{(k_3 - k_2)}{(2k_2 - k_3)}e^{-k_3t} + \frac{1}{2} + \left(\alpha_{22(0)} - \alpha_{20(0)}\frac{(k_3 - k_2)}{(2k_2 - k_3)} - \frac{1}{2}\right)e^{-2k_2t} \quad (4)$$

Two sets of exemplary kinetic data appear in Tables III and IV. The entire kinetic and thermodynamic profiles for the electrocyclic ring opening of **12** ≈ **20** and for bond shifting in **7** ≈ **22** ≈ **23** follow in Table V. Finally, the energetics of ring inversion are computed from k_{rac} and k_2 in Table VI.

Discussion

The experiments reported here bear on the energetics of electrocyclic ring opening of bicyclo[4.2.0]octatraene **12** ≈ **20**, the energetics of ring inversion in **7**, and the energetics of bond shifting within the 1,3-di-*tert*-butyl COT framework. While the range of data provides compelling mechanistic information, the three processes in question are not so interdependent that they must be discussed as a unit. For the sake of clarity, therefore, the dynamic behavior of the title compounds is dissected into its distinctive components.

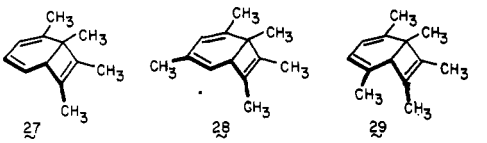
Valence Isomerization. Diels–Alder cycloadditions to cyclooctatetraenes and its derivatives are frequently preceded by disrotatory ring closure to bicyclo[4.2.0]octatrienes. This phenomenon is observed, despite the requisite surmounting of an added energy barrier, because such bicyclic intermediates offer a quasiplanar conjugated diene segment which greatly facilitates dienophile capture. For the parent hydrocarbon, Huisgen and his co-workers have determined the energy of activation for cyclization to **26** (k_{-3}) to be 27.2 kcal/mol (ΔH^{*} = 27.4–28.1



25 26

kcal/mol).[33,34] For monosubstituted cyclooctatetraenes, the presence of an R group has been found to decrease somewhat the barrier of electrocyclization (R = C_6H_5, $\Delta H^{\ddagger}$ = 24.5 kcal/mol[35]) and to exert observable influences on the favored bicyclooctatriene substitution plan.[30,36,37]

Increased levels of alkyl substitution *sometimes* is accompanied by an enhanced thermodynamic stability of the bicyclic valence tautomer. In the case of 1,2,3,4-Me_4COT (but not 1,2,3,8-Me_4COT), an equilibrium concentration of 25% for **27** is seen



27 28 29

at room temperature.[14] While the 1,2,3,4,6-Me_5 derivative behaves comparably (**29** > **28**), its 1,2,3,5,8-Me_5 bond shift isomer gives no evidence of inhomogeneity within the limits of spectroscopic analysis.[14] The fully substituted octamethyl derivative has been described by Criegee as having greater stability than its [8]-annulene counterpart.[38] Clearly, adequately high levels of peripheral steric strain can be offset in part by suitable electrocyclization. The bicyclo[4.2.0]octatriene ring system can also be stabilized by bracketing across C-1 and C-4, provided that the number of atoms in the bridge is sufficiently small.[39]

While a reasonable appreciation of various structural effects on k_{-3} are now available, Vogel's pioneering experimental assessment of the **26** → **25** ring opening (E_{act} = 18.7 kcal/mol) has stood alone for almost 2 decades.[40] One limiting factor in the determination of k_3 has been the availability of bicyclo[4.2.0]-octatriene derivatives; however, several compounds of this general type are now known.[39,41-44] In the case of **26**, the half-life at 0 °C is but 14 min.[40] We now find that attachment of a pair of *tert*-butyl groups to C-2 and C-4 as in **12** ≈ **20** leads to a substantive increase in the activation parameters relative to **26**: E_{act} = 28.4 kcal/mol and $\Delta H^{\ddagger}$(25 °C) = 27.8 kcal/mol (Table V). The increase in activation energy would appear to arise chiefly from those steric considerations which come into play in the transition state associated with disrotatory cleavage of the central bond.

The Diels–Alder cycloaddition of *N*-phenyltriazolinedione to **7** which results in the formation of **14** shows that kinetically controlled cycloaddition to this system prefers valence tautomer **30**. This is as expected since **30** contains an unsubstituted diene

30

unit and accordingly offers no steric inhibition to dienophile capture from that direction. The relative importance of valence isomers **12** and **30** in the absence of a trapping agent has not been determined. What is clear is that their concentration levels are too low under ordinary conditions to be detectable.

Ring Inversion Barrier. Since 1,3-(t-Bu)$_2$COT is capable of isolation in optically active form, the magnitude of the barrier to its ring inversion must be adequately high to restrict the molecule from readily attaining a planar conformation. The E_{act} of 19.9 kcal/mol, $\Delta H^{\ddagger}$(25 °C) of 19.3 kcal/mol, and $\Delta G^{\ddagger}$(25 °C) of 21.6 kcal/mol determined for **7** indicate that its potential functions for torsional strain and bond angle deformation exceed

(33) (a) Huisgen, R.; Mietzsch, F. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 83. (b) Huisgen, R.; Mietzsch, F.; Boche, G.; Seidl, H. *Chem. Soc., Spec. Publ.* **1965**, *No. 19*, 3.
(34) Huisgen, R., private communication.
(35) Huisgen, R.; Konz, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 4102.
(36) (a) Huisgen, R.; Konz, W. E.; Gream, G. E. *J. Am. Chem. Soc.* **1970**, *92*, 4105. (b) Gasteiger, J.; Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *8*, 716. (c) Huisgen, R.; Konz, W. E.; Schnegg, U. *Ibid.* **1972**, *8*, 715.
(37) Paquette, L. A.; Kitching, W.; Heyd, W. E.; Meisinger, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 7371.
(38) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 519.
(39) (a) Paquette, L. A.; Philips, J. C. *J. Chem. Soc., Chem. Commun.* **1969**, 680. (b) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4516.
(40) Vogel, E.; Kiefer, H.; Roth, W. R. *Angew Chem., Int. Ed. Engl.* **1964**, *3* 442.
(41) (a) McCay, I. W.; Warrener, R. *Tetrahedron Lett.* **1970**, 4779, 4783. (b) Warrener, R.; McCay, I. W.; Tan, R. Y. S.; Russell, R. A. *Ibid.* **1979**, 3183.
(42) Sket, B.; Zupan, M. *J. Am. Chem. Soc.* **1977**, *99*, 3504.
(43) Bryce-Smith, D.; Gilbert, A.; Orgen, B. H.; Twitchett, P. J. *J. Chem. Soc., Perkin Trans. 1* **1978**, 232.
(44) Hanzawa, Y.; Paquette, L. A., following paper in this issue.

those of various monosubstituted derivatives [$\Delta G^{\ddagger}$(−25 to 0 °C) = 12.7–14.7 kcal/mol][5,6] by a reasonable margin. When compared to the constraints operative in the 1,2,3-Me_3COT example [E_{act} = 23.0 kcal/mol, $\Delta H^{\ddagger}$(25 °C) = 22.4 kcal/mol, $\Delta G^{\ddagger}$(25 °C) = 24.7 kcal/mol], the 1,3-(*t*-Bu)$_2$ substitution plan is seen to occupy an intermediate position.

A total energy increase of 15.1 kcal/mol has been computed for flattening the unsubstituted cyclooctatetraene framework into an optimized D_{4h} planar geometry.[6] This barrier, which materializes as a consequence of increases in van der Waals and angular bending energies, can be considered to be a common element in the ring inversion of all cyclooctatetraenes. Consequently, the differences which appear in the $\Delta G^{\ddagger}_{RI}$ values for variously substituted COTs arise chiefly from steric compression of the peripheral substituents in the transition state. For **7**, the enhanced level of nonbonded steric interaction involving the noncontiguous *tert*-butyl groups on C-1 and C-3 and the flanking ring hydrogen atoms in the transition state is the main cause of the increase in the energy barrier. In the tub conformation of **7**, the *tert*-butyl substituents are likely freely rotating. Such motions appear substantively more restricted in planar alternate transition state **31**, as reflected in the rather negative $\Delta S^{\ddagger}$(25 °C) term (−7.5 eu).

31 **32**

The ca. 6.5 kcal/mol of added RI destabilization energy associated with **31** is transferable within narrow limits to the transition state for bond shifting (**32**) since both structures share the common feature of [8]annulene planarity.

Bond Shifting Energetics. As commonly observed, the barrier to bond shifting in **7** lies above that due to ring inversion. Although the activation energy and enthalpy (25 °C) associated with BS in **7** (23.3 and 22.7 kcal/mol, respectively) compare closely to the corresponding activation parameters for the 1,2,3-Me_3COT system (23.5 and 22.9 kcal/mol),[15d] the corresponding free energy changes are rather more divergent (23.6 vs. 26.5 kcal/mol) because of entropic influences (−2.9 vs. −12 eu). That the three vicinal methyl groups experience higher levels of steric constraint than the *tert*-butyl groups in **32** is as expected.

To the extent that the delocalization energy associated with **32** can be approximated by the relationship

$$E_D = \Delta H^{\ddagger}_{RI} - \Delta H^{\ddagger}_{BS}$$

delocalization of the 8π electrons in **7** is seen to be destabilizing by 3.4 kcal/mol. In 1965, Dewar and Gleicher described PPP and SPO MO calculations which led them to conclude that E_R within a D_{8h} perimeter such as **32** should be antiaromatic by 4 kcal/mol;[45] later, more sophisticated calculations led to a widely variant conslusion (15.4 kcal/mol)[10] which has received no experimental support.

The implications of the present and earlier results should now be made clear. Of the forces operating in progressing from the ground-state tub conformation of **7** to planar-delocalized transition state **32**, angle strain, van der Walls repulsions, and related phenomena contribute ca. 85% of the enthalpy demands. The remaining 15% can be traced to resonance destabilization. Consequently, the driving force behind COT nonplanarity has minimal to do with the energetics of antiaromatic conjugation. This is not to say that COT is not antiaromatic, for the [8]-annulene ring system is unquestionably so. However, the antiaromaticity level is weak and incapable of dominating the overall conformational energetics.

One must be careful not to equate the concept of antiaromaticity with the tendency to be nonplanar. Figure 3 may serve to illustrate matters more clearly. In a planar polyene system which is shown at the lower left, there will exist electronic contributions appropriate to cause the substance to be either aromatic, nonaromatic,

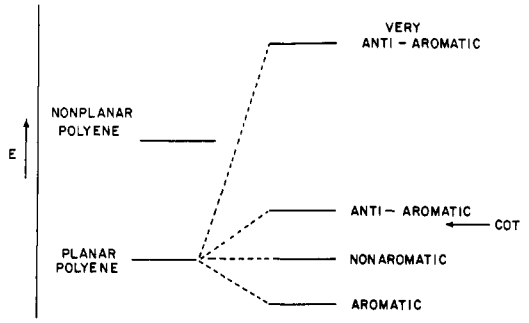


Figure 3. Energetic ordering of planar and nonplanar polymers characterized by different electronic features.

or antiaromatic. The possibility also exists that the molecule is very antiaromatic as shown in the upper right. Given the latter circumstance, the system would rather be nonplanar because the antiaromaticity overwhelms the tendency for planarity. In cyclooctatetraene, the level of antiaromaticity is sufficiently low that the π network would prefer to be planar and delocalized. Actually, the relative magnitude of the antiaromaticity is so much less than the energy required to twist about the single bonds that the molecule is forced to be puckered. This behavior is in contrast to that exhibited, for example, by 1,5-bisdehydro[12]annulene where the antiaromatic π delocalization energy is more dominant and the system adopts an essentially planar conformation.[12]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian T-60 and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were also recorded on the Bruker unit. Mass spectra were measured with an AEI-MS9 spectrometer at an ionization energy of 70 eV. Polarimetric measurements were made with a Perkin-Elmer Model 241 polarimeter. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***endo*-1,7-Di-*tert*-butyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dione (10).** To a cold (−5 °C) stirred solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (**9**, 0.60 g, 2.72 mmol) and cyclobutadieneiron tricarbonyl (0.58 g, 3.0 mmol) in dry acetone (45 mL) under nitrogen was added 8.2 g (0.015 mol) of ceric ammonium nitrate in small portions at approximate 5-min intervals. In each instance, carbon monoxide evolution had ceased before the next portion was introduced. When the addition was complete, ether (200 mL) was added and the precipitated solids were removed by filtration through Celite. The filtrate was washed with water (5 × 150 mL), dried, and evaporated to dryness. The residual brown oil was crystallized from hexane to give 0.38 g (51%) of yellow crystals, mp 120–122 °C: IR (KBr, cm^{-1}) 1743, 1730, 1479, 1462, 1379, and 1366; UV (pentane) λ_{max} 240 (ϵ 575) and 300 nm (20); ^{1},h NMR (δ, $CDCl_3$) 6.0–5.75 (m, 3 H), 3.6–3.38 (m, 1 H), 3.34–3.12 (m, 2 H), 1.14 (s, 9 H), and 0.98 (s, 9 H); *m/e* calcd 272.1776, obsd 272.1783.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.29; H, 8.84.

Generation and Trapping of 2,4-Di-*tert*-butylbicyclo[4.2.0]octa-2,4,7-triene (12). A solution of **10** (480 mg, 1.77 mmol) in 5 mL of chloroform was placed in a Pyrex tube and cooled in an ice–water bath while irradiated with a 200-W Hanovia lamp. After 2.5 h, a solution of *N*-phenyltriazolinedione in the same solvent was added dropwise until the red color of the dienophile persisted. Following the removal of solvent, the residual oil was purified by preparative layer chromatography on silica gel (elution with hexane–ether, 3:1). In addition to 36 mg of recovered **10**, there was isolated 83 mg (12%) of adduct **13** as colorless crystals, mp 161–162 °C (from ether–hexane): ^{1}H NMR (δ, $CDCl_3$) 7.47–7.17 (m, 5 H), 6.0–5.85 (m, 3 H), 5.28–5.12 (m, 2 H), 3.55–3.27 (m, 2 H), 1.37 (br s, 9 H), and 1.13 (s, 9 H); *m/e* calcd 391.2259, obsd 391.2267.

Anal. Calcd for $C_{24}H_{29}N_3O_2$: C, 73.63; H, 7.47. Found: C, 73.66; H, 7.55.

1,3-Di-*tert*-butylcyclooctatetraene (7). A cold (0 °C) solution of **10** (0.50 g) in chloroform was irradiated for 1 h with a 450-W Hanovia lamp. The solvent was evaporated under reduced pressure to leave an orange-yellow oil. The above operation was repeated until the total amount of **10** utilized reached 11.133 g. The combined oily product was chromatographed on silica gel (hexane elution) to give 7.46 g (84%) of **7** as a colorless liquid: ^{1}H NMR (δ, $CDCl_3$) 6.08–5.37 (m, 6 H), 1.08

(45) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685.

(s, 9 H), and 1.05 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 153.66, 150.86, 132.61, 132.32, 130.42, 130.00, 123.41, 120.90, 36.55, 36.27, 29.87, and 29.77; *m/e* calcd 216.1878, obsd 216.1874.

Diels–Alder Reaction of 7 with *N*-Phenyltriazolinedione. To a solution of **7** (1.54 g, 0.007 mol) in 50 mL of ethyl acetate was added 2.5 g (0.014 mol) of *N*-phenyltriazolinedione. The reaction mixture was heated at the reflux temperature for 1 h, cooled, and evaporated to dryness. The residue was chromatographed on Florisil (ether elution), and 830 mg (30%) of **14**, colorless crystals, mp 149–150 °C (from ether–hexane), was isolated: ^1H NMR (δ, $CDCl_3$) 7.38 (m, 5 H), 6.3 (ddd, J = 7, 6.5, and 2 Hz, 1 H), 5.94 (ddd, J = 6.5, 6.5, and 1.5 Hz, 1 H), 5.60 (d, J = 2 Hz, 1 H), 5.2–4.82 (m, 2 H), 3.12 (dd, J = 4.5 and 2 Hz, 1 H), 1.13 (s, 9 H), and 1.02 (s, 9 H); *m/e* calcd 391.2260, obsd 391.2265.

Anal. Calcd for $C_{24}H_{29}N_3O_2$: C, 73.63; H, 7.47. Found: C, 73.67; H, 7.44.

Hydrolysis–Oxidation of 13. A mixture of **13** (171 mg, 0.4 mmol) and sodium hydroxide (350 mg) in isopropyl alcohol was heated at the reflux temperature under nitrogen for 24 h. After cooling, the mixture was acidified with 3 N hydrochloric acid, then rendered slightly alkaline by careful addition of 3 N ammonium hydroxide solution. Activated manganese dioxide (300 mg) and petroleum ether (20 mL) were added and the mixture was stirred for 30 min before being poured into ice–water and extracted with ether. The organic phase was washed with brine, dried, and evaporated to leave a pale yellow oil which was eluted through a short Florisil column (hexane solvent). There was obtained 90 mg (~100%) of **7**, the spectral properties of which were identical with those of the authentic sample.

Hydrolysis–Oxidation of 15. A mixture of **15** (349 mg, 0.90 mmol) and sodium hydroxide (400 mg) in isopropyl alcohol (20 mL) was heated at reflux temperature under nitrogen for 17 h. Further processing in the predescribed manner ultimately afforded 165 mg (86%) of **7**.

Diels–Alder Reaction of 7 with (–)-*endo*-Bornyltriazolinedione (15*). To a refluxing solution of **7** (7.46 g, 0.035 mol) in ethyl acetate (150 mL) was added dropwise under nitrogen a solution of **15*** (8.23 g, 0.035 mol) in ethyl acetate (70 mL). After completion of the addition, heating was continued for an additional 20 h. The solvent was evaporated and the residual pink oil was eluted through Florisil (elution with ether–hexane, 10:1) to give 8.75 g (55%) of a mixture of **16*** and **17*** as a pale yellow oil, $[\alpha]^{23}_D$ –4.2°, $[\alpha]^{23}_{578}$ – 4.4° $[\alpha]^{23}_{546}$ –4.8°, $[\alpha]^{23}_{436}$ –6.0° (*c* 9.6, C_2H_5OH).

Crystallization of the mixture was effected in hexane. There was isolated 1.76 g (11% from **7**) of colorless solid, mp 150–165 °C, $[\alpha]^{23}_D$ +7.5°, $[\alpha]^{23}_{578}$ +8.0°, $[\alpha]^{23}_{546}$ +9.5°, $[\alpha]^{23}_{436}$ +19.8° (*c* 8.6, C_2H_5OH).

Five recrystallizations of this material, first from hexane and later from hexane–ether, gave 156 mg of optically pure **17*** as colorless crystals, mp 167.5–169 °C: $[\alpha]^{23}_D$ +56.6°, $[\alpha]^{23}_{578}$ +59.4°, $[\alpha]^{23}_{546}$ +68.7°, $[\alpha]^{23}_{436}$ +129° (*c* 6.7, C_2H_5OH); ^1H NMR (δ, $CDCl_3$) 6.26 (ddd, J = 7, 6.5, and 1.5 Hz, 1 H), 5.9 (ddd, J = 6.5, 6.0, and 1.5 Hz, 1 H), 5.6 (d, J = 2 Hz, 1 H), 5.1–4.73 (br m, 2 H), 4.4–3.9 (br m, 1 H), 3.07 (dd, J = 5 and 2 Hz, 1 H), 2.6–1.2 (series of m, 7 H), 1.1 (s, 9 H), 1.0 (s, 12 H), 0.87 (s, 3 H, and 0.78 (s, 3 H).

Anal. Calcd for $C_{28}H_{41}N_3O_2$: C, 74.46; H, 9.15; N, 9.30. Found: C, 74.37; H, 9.13; N, 9.32.

Determination of the Diastereomeric Purity of 16*/17*. A 39.2-mg sample of diastereoisomer mixture **16*/17***, $[\alpha]^{23}_D$ +7.5° (*c* 8.6, C_2H_5OH) was dissolved in $CDCl_3$ and the ^1H NMR spectrum was recorded. Particular attention was focused on the two *tert*-butyl signals at δ 1.1 and 1.0. To this sample was added 7.1 mg (0.11 mol equiv) of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III), and the ^1H NMR spectrum was again recorded. The singlet originally at δ 1.0 was now seen as two singlets at δ 1.05 and 1.0 (the originally underlying methyl signal had shifted to 1.16) while that at δ 1.1 now appeared as two peaks at 1.3 and 1.1. From a series of such experiments, it was revealed that the levorotatory diastereoisomer was the source of the 1.1 and 1.0 signals while the dextrorotatory compound displayed the 1.3 and 1.05 peaks. For integration purposes, expanded scale spectra were recorded and a planimeter was utilized. The following data are representative (see Figure 1):

$[\alpha]_D^{23}$	% levorotatory	% dextrorotatory
–12.6°	54.5	45.5
+7.5°	34.1	65.9
+52.6°	2	98

General Procedure for Hydrolysis–Oxidation of 16*/17*. To a solution of the *endo*-bornyltriazolinedione adduct (150 mg) in dimethyl sulfoxide (30 mL) under nitrogen was added 1.2 g of powdered potassium *tert*-butoxide in one portion, and the reaction mixture was stirred at room temperature for 30–40 h. The solution was poured into ice–water and acidified to pH 2 with concentrated hydrochloric acid. After the acidic solution had been stirred at room temperature for 30 min, the mixture was cooled in an ice bath, made alkaline with concentrated ammonium hydroxide solution, and extracted with ether (3 × 50 mL). The combined organic layers were washed with water and brine prior to drying. The filtered ether solution was cooled to –70 °C and treated with a 10-fold molar excess of activated manganese dioxide. The mixture was stirred for 30–40 min under nitrogen, rapidly filtered into a cold receiver flask, and evaporated at 0 °C. The residual oil was chromatographed on a Florisil column to –45 to –40°C (pentane elution). The first and second fractions (~60 mL in size) contained the cyclooctatetraene (10–20 mg). These were evaporated as before and the [8]annulene was employed directly in the racemization kinetic studies. ^1H NMR examination revealed the product to be pure **7***.

Determination of Racemization Rates. The following urazole samples were utilized: (a) –3 °C, run 1: $[\alpha]^{23}_D$ –55° (*c* 3.2 mg, C_2H_5OH) or 85% levorotatory; (b) –3 °C, run 2: $[\alpha]^{23}_D$ –63.7° (c 4.1 mg, C_2H_5OH) or 95% levorotatory; (c) 11.5 °C, runs 1 and 2: $[\alpha]^{23}_D$ –55°; (d) 18.5 °C, runs 1 and 2: $[\alpha]^{23}_D$ –55°.

The sample of **7*** produced as indicated above was immediately dissolved in cold (–10 °C) ethanol and transferred to the thermostated polarimeter tube (1 dm). The solution was allowed to equilibrate for a few minutes at which point an accurate timer was started and readings were taken at appropriate time intervals. The slopes of the mean plots of $-\ln \alpha$ vs. time were determined by a linear least-squares analysis of the experimental data points in each case. Exemplary data are given in Table II. In each experiment, the infinity point read 0°. Evaporation of solvent from each of the solutions was followed by thin layer chromatography and ^1H NMR analysis of the residual oil. This material was determined to be pure racemic 1,3-di-*tert*-butylcyclooctatetraene with no evidence of impurity contamination.

Tetradeuteriocyclobutadieneiron Tricarbonyl (18). Trifluoroacetic acid-*d* was prepared in situ by addition of 100% deuterium oxide (2.2 g, 0.11 mol) to purified (P_2O_5 dried) trifluoroacetic anhydride (23.1 g, 0.11 mol) with ice cooling under an argon atmosphere. Cyclobutadieneiron tricarbonyl was introduced dropwise while the solution was magnetically stirred, and stirring was maintained at room temperature for 1.5 h. The reaction mixture was transferred by syringe into an ice–water mixture. Hexane (50 mL) was added, the mixture was stirred vigorously, and the organic layer was separated. All of these operations were conducted under argon. The extraction was repeated (3 × 10 mL) and the combined organic layers were washed well with saturated sodium carbonate solution prior to drying and solvent evaporation. Four additional identical runs were carried out and the resulting orange oil was further purified by alumina chromatography (pentane elution. There was obtained 2.47 g (48%) of **18**. The deuterium content was shown to be 88% of d_4 by repeated ^1H NMR integration of $CDCl_3$ solutions containing carefully weighed amounts of toluene as internal standard.

***endo*-1,7-Di-*tert*-butyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dione-*2,3,4,5-d*$_4$ (19).** Reaction of 4.4 g (0.02 mol) of *o*-quinone **9** (4.40 g, 0.02 mol) with complex **18** (2.4 g, 0.013 mol) and ceric ammonium nitrate (36 g, 0.066 mol) according to the predescribed conditions afforded **19** (2.0 g, 56%) as yellow crystals, mp 118–120 °C (from hexane): ^1H NMR (δ, CCl_4) 6.08 (d, J = 2 Hz, 1 H), 3.63 (d, J = 2 Hz, 1 H), 1.14 (br s, 9 H), and 0.98 (s, 9 H).

Generation and Trapping of 2,4-Di-*tert*-butylbicyclo[4.2.0]octa-2,7-triene-*1,6,7,8-d*$_4$. Two solutions of **19** (49.3 and 49.0 mg) in chloroform (1 mL) were simultaneously irradiated in the manner outlined above, and *N*-phenyltriazolinedione was added to the combined reaction mixtures until a pink color persisted. Silica gel chromatography permitted the isolation of **21** (21 mg) and recovered **19** (60 mg). For **21**: ^1H NMR (δ, $CDCl_3$) 7.47–7.17 (m, 5 H), 5.92 (d, J = 2 Hz, 1 H), 5.2 (d, J = 2 Hz, 1 H), 1.37 (br s, 9 H), and 1.15 (s, 9 H).

For the kinetic studies to be described, the photolysis was carried to completion. The following procedure is prototypical. A solution of **19** (25 mg) in $CDCl_3$ (0.5 mL) contained in an NMR tube cooled in an ice–water bath was irradiated with a Hanovia 200-W lamp for 3.5 h. The ^1H NMR spectrum was recorded and only the olefinic proton signals at δ 5.7 and 5.23 due to **20** were in evidence. After the tube had been stored at 35–40 °C for 1.5 h, the formation of **22** ⇄ **23** was seen to be well advanced.

Hydrolysis–Oxidation of 21 and 25. To a mixture of potassium *tert*-butoxide (800 mg) in dry dimethyl sulfoxide (20 mL) was added 150 mg of **21**, and the mixture was stirred at room temperature for 40 h under nitrogen. The solution was poured into ice–water, made acidic by addition of concentrated hydrochloric acid, and rebasified with ammonium hydroxide. This mixture was extracted with ether and the organic phase was washed with brine prior to drying. The ether solution was cooled to –70 °C, treated with activated manganese dioxide (400 mg), and stirred for 30 min. Filtration and evaporation of solvent left an oil which

was passed through a cold (−40 °C) Florisil column (elution with hexane). There was obtained a colorless oil, the ^1H NMR spectrum of which showed it to be a mixture of **20**, **22**, and **23** (ratio differed somewhat from run to run).

Comparable treatment of **24** afforded a mixture of **22** and **23** in a 1:1 ratio.

Procedure for Determining the Rates of Electrocyclic Ring Opening in 20 and Bond Shifting in 22 ⇄ 23. A small amount (about 25 mg) of the hydrocarbon prepared as above was dissolved in $CDCl_3$ and transferred to an NMR tube. The solution was degassed by three freeze–thaw cycles, sealed under vacuum, and placed in the thermally equilibrated constant-temperature probe of a Bruker HX-90 NMR spectrometer. After allowance was made for thermal equilibration (several minutes), FT spectra (four scans) were taken at appropriate time intervals. The olefinic proton region was recorded on fully expanded scale and the peaks were machine integrated.

Estimated values of the rate constants k_2 and k_3 were obtained using a nonlinear least squares fit of eq 4 to be experimental data. In this procedure, a measure of "goodness of fit" χ^2 was minimized with respect to each of the parameters k_2 and k_3 simultaneously (eq 5). The calcu-

$$\chi^2 = \sum\{[y_i - y_i(\chi_i)]^2/\sigma_i^2\} \quad (5)$$

lations were carried out using an appropriately modified version of the routine CURFIT.[46]

Single-Crystal X-ray Analysis of 17*. A single crystal ~0.3 mm^3 was chosen for diffraction work. Preliminary X-ray photographs showed orthorhombic symmetry. Accurate lattice constants, obtained by a least-squares fit of 15 moderate 2θ values, were: **a** = 10.8527 (9), **b** = 15.1095 (13), and **c** = 15.9280 (13) Å. Systematic extinctions and the presence of chirality were uniquely accommodated by space group $P2_12_12_1$ and density considerations suggested one molecule of composition $C_{28}H_{41}N_3O_2$ formed the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using a variable speed, 1° ω-scan and graphite monochromated Cu Kα radiation (1.54178 Å). Of the 2043 reflections collected in this manner, 1969 (95%) were judged observed after correction for Lorentz, polarization, and background effects ($F_o^2 \geq 3\sigma(F_o^2)$).

A phasing model was achieved using a multisolution weighted tangent formula approach in which four special and one general reflection served as a starting set for 200 E's.[47] An E synthesis calculated from the most favorable solution showed 30 plausible nonhydrogen atoms. The remaining nonhydrogen atoms were found on a subsequent F synthesis and the hydrogens on a ΔF synthesis after partial refinement. Full-matrix, least-squares refinements with anisotropic nonhydrogen atoms and fixed isotropic hydrogens have currently converged to a standard crystallographic residual of 0.095. Further crystallographic information can be found in the Supplementary Material.

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Supplementary Material Available: Racemization rate data and activation parameters for (+)-**7**, polarimetric data obtained for the racemization of (+)-**7***, exemplary rate data for the conversion **20** → **22** ⇌ **23** at 36 °C and 46 °C, bicyclooctatriene electrocyclic ring opening and bond shifting rate data for **12** ≈ **20** and **7** ≈ **22** ≈ **23**, a compilation of racemization, bond shifting, and ring inversion rate data for 1,3-(t-Bu)$_2$COT, and fractional coordinates, temperature factors, bond distances, bond angles, and structure factors for **17*** (17 pages). Ordering information is given on any current masthead page.

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Bond Fixation in Annulenes. 12. Effect of Vicinal Di-*tert*-butyl Substitution on Cyclooctatetraene Valence Isomerization. 7,8-Di-*tert*-butylbicyclo[4.2.0]octa-2,4,7-triene[1]

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Abstract: 7,8-Di-*tert*-butylbicyclo[4.2.0]octa-2,4,7-triene (**3**) has been prepared by Diels–Alder addition of cyclobutadiene to 3,4-di-*tert*-butylcyclopentadienone and pyrolysis of the adduct. Because of unusually high levels of peripheral steric strain, **3** does not undergo observable ring opening to the cyclooctatetraene. This example is the first where the less stable [8]annulene valence tautomer is seen to be thermodynamically favored in the absence of constraining influences (e.g., bridged systems). Flash vacuum pyrolysis of the title compound at 550 °C gave both bond shift isomers of 1,4-di-*tert*-butylcyclooctatetraene.

During the past 2 decades, studies conducted in several leading international laboratories have demonstrated that cyclooctatetraene is capable of three fundamental structural changes, the energetic demands of which for the parent hydrocarbon fall in the order: ring inversion < bond shifting ≪ valence isomerization.[3,4] While the first two phenomena are related in their common dependence on the attainment of a planar transition state, the conversion to bicyclo[4.2.0]octa-2,4,7-triene requires disrotatory cyclization of three contiguous double bonds. Despite the richness of cyclooctatetraene's dynamic behavior, little attention has previously

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