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Steric Acceleration of Dynamic Processes in 1,2-Dicyclooctatetraenylbenzene

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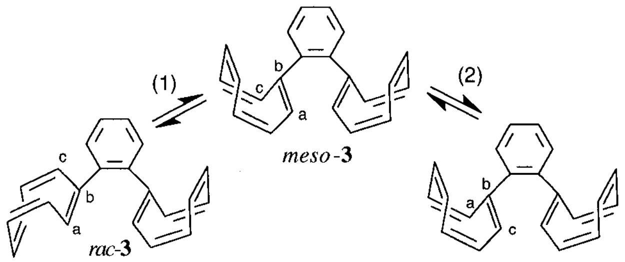
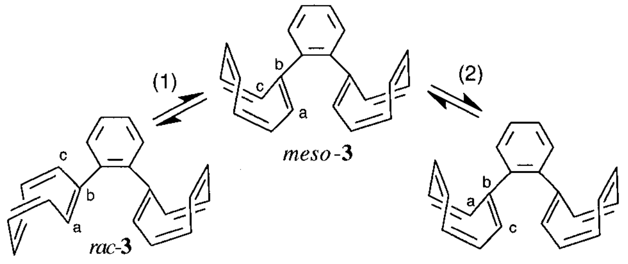
ABSTRACT

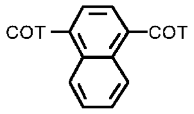


The rate constants for ring inversion (1) (at −31 °C) and bond shift (2) (at 19 °C) in the title compound (3) are 3–5 and 2 times the corresponding values for the 1,4 isomer due to steric hindrance in the ground state of 3.

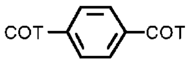
Cyclooctatetraene (COT) is known to undergo the dynamic processes of ring inversion (eq 1) and bond shift (eq 2), both of which can be studied by dynamic NMR spectroscopy.[1]



We have recently shown that the rates of these reactions are increased in 1,4-dicyclooctatetraenylnaphthalene (**1**) relative to 1,4-dicyclooctatetraenylbenzene (**2**).[2] This result was attributed to a greater steric hindrance in the ground state of **1** relative to **2**, as evidenced by a greater calculated (HF/3-21G) torsional angle between the C_1C_2 double bond in the COT ring and the aryl ring of 1-naphthylCOT than phenylCOT, which are models for inter-ring interactions in **1** and **2**, respectively. However, this conclusion was necessarily an indirect one because the total energies of **1** and **2** cannot be directly compared due to the fact that they are not isomers. In fact, the inability to distinguish between ground and transition state effects is a general problem in establishing the phenomenon of steric acceleration.



1



2

In the present paper, we test our hypothesis of steric acceleration of ring inversion and bond shift by investigating the sterically compressed molecule 1,2-dicyclooctatetraenylbenzene (**3**).[3] Since **2** and **3** are isomers, comparison of the calculated total energies of their ground states and ring inversion transition states should reveal the origin of any steric effects that are suggested by kinetic studies.[4]

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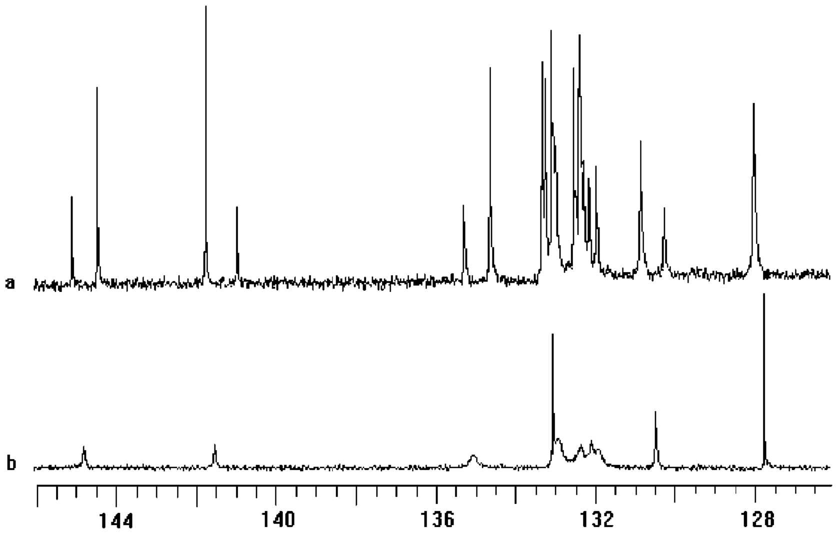

Figure 1. ^{13}C NMR spectra of **3** in THF-d_8 at 75 MHz: (a) −65 °C; (b) 25 °C.

Monosubstituted cyclooctatetraenes are chiral moieties. Consequently, **3** exists as a pair of diastereomers that can be interconverted through ring inversion. Because of the proximity of the two COT rings in **3**, the ^{13}C signals for corresponding carbons in the two diastereomers are well separated in the slow exchange region (Figure 1a). It can be estimated from the relative peak heights that the two diastereomers exist in a ratio of 1:2, corresponding to a ΔG_{isom} of 0.3 kcal/mol at −65 °C. The racemic isomer (*rac*-**3**) is calculated to 0.4 kcal/mol more stable than the meso isomer (*meso*-**3**) on the basis of geometry optimizations at the HF/3-21G level (Table 1).[5,6]

Table 1. Geometry Optimization of Ground States and Ring Inversion Transition States of **2** and **3**[a]

compd	state[b]	rel energy[c]	$\omega(C_2C_1C_{1'}C_{2'})$[d]
2[e]	GS	0	43.1, 43.1
	TS	19.0	43.2, 61.7[f]
rac-**3**	syn GS	0[g]	66.8, 116.7
	anti GS	0.51	−105.0, −104.9
meso-**3**	syn GS	0.40	116.0, −55.7
	anti GS	0.40	114.7, 107.3
3	syn TS	18.3	−52.3, 118.1[f]
	anti TS	18.5	−104.9, −107.5[f]

[a] HF/3-21G calculations. [b] Syn and anti refer to the relative orientations of the C_1C_2 double bonds in the two COT rings with respect to the plane of the phenylene ring. [c] $\Delta(E+ZPE)_{\text{ri}}$ in kcal/mol relative to the lowest energy conformer of **2** or **3**. [d] Dihedral angle between C_1C_2 of the COT ring and $C_{1'}C_{2'}$ of the phenylene ring. [e] Lowest energy conformers are PM/anti/anti′ in the GS and syn/anti′ in the TS.[2] [f] Planar COT ring. [g] Relative energy with respect to the ground state of **2** is 3.1 kcal/mol.

Rate constants for the interconversion of diastereomers (k_c) were determined from exchange broadening at < −30 °C for two different samples. As seen in Figure 1a, four pairs of signals (δ 145, 141, 135, and 130) were sufficiently separated to permit investigation of their exchange broadening. The value of k_c was calculated from eq 3,[7]

$$k_c = \pi \Delta W_{\text{ex}} \tag{3}$$

where ΔW_{ex} is the exchange broadening of a signal (in hertz) in the region of slow exchange. Since diastereomers can interconvert through either ring inversion or bond shift, k_c is given by eq 4.[8]

$$k_c = k_{\text{ri}} + k_{\text{bs}}/2 \tag{4}$$

The value of k_{bs} could not be measured over a large enough temperature range for extrapolation to temperatures at which k_c could be determined. Therefore, k_{ri} is only reported for −31 °C (Table 2), where one can reasonably assume that $k_{\text{ri}} \approx k_c$.

Table 2. Kinetic Data for Ring Inversion and Bond Shift in **2** and **3**

compd	process	temp range (K)	k[a]	T (K)	$\Delta G^{\ddagger}$[b]
2[c]	RI	233−244	2.6	242	13.5
	BS	271−298	19.4	292	15.2
3	RI	242	13.5[d]	242	12.8[d]
			8.6[e]		13.1[e]
	BS	282−292	38.0	292	15.0

[a] In s^{-1}, ±20%. [b] ±0.1 kcal/mol. [c] Reference 2. [d] *meso*-**3**. [e] *rac*-**3**.

Bond shift rate constants (k_{bs}) were determined for two samples at temperatures sufficiently high to minimize line broadening due to interconversion of diastereomers. The only signal broadened by bond shift exchange that does not overlap with other peaks is the one at δ 135 (Figure 1b).

Any residual broadening of this peak due to k_c was corrected for by subtracting the line width of the peak at δ 145. The use of the latter signal is appropriate because the chemical shift difference between the corresponding signals of the two diastereomers at −65 °C (0.64 ppm) is nearly identical to that for δ 135 (0.66 ppm).

As seen in Table 2, $\Delta\Delta G^{\ddagger}_{\mathrm{ri}}$ ($\Delta G^{\ddagger}_{\mathrm{ri}}(\mathbf{2}) - \Delta G^{\ddagger}_{\mathrm{ri}}(\mathbf{3})$) and $\Delta\Delta G^{\ddagger}_{\mathrm{bs}}$ are ca. 0.5 and 0.2 kcal/mol, respectively; values that are similar to those found for the comparison of **1** and **2**. The origin of this result is revealed by geometry optimizations of the ground states and ring inversion transition states of **2** and **3** (Table 1). First, note that the interring torsional angles are ca. 20 and 24° greater in the ground state of **3** compared to **2** but only 9 and 0° greater in the ring inversion transition state. (The bond shift transition state is expected to be sterically similar to the latter but cannot be calculated because of the size of the molecules and the multiconfiguration wave function required.[4,9]) In addition, the total energy (E+ZPE) of the ground state of **3** is 3.1 kcal/mol greater than that of **2** while the corresponding ring inversion transition states differ by only 2.4 kcal/mol. The close agreement of the experimental and calculated values of $\Delta\Delta G^{\ddagger}_{\mathrm{ri}}$ (0.5 and 0.7 kcal/mol, respectively) supports the validity of the latter. Thus, these calculations confirm the assumption that an increase in the twist angle parallels an increased steric strain in these molecules as well as the hypothesis that *the greater rate of ring inversion and bond shift in* ***3*** *compared to* ***2*** *primarily arises from increased steric strain in the ground state of* ***3****.*

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(3) **1,2-Dicyclooctatetraenylbenzene (3).** To a solution of 1,2-diiodobenzene (0.792 g, 2.40 mmol), Pd_2dba_3 (0.114 g, 0.125 mmol), and $AsPh_3$ (0.153 g, 0.500 mmol) in 25 mL of dry NMP at rt was added cyclooctatetraenyltrimethylstannane (1.339 g, 5.00 mmol) in 5 mL of dry NMP. After 24 h the reaction mixture was diluted with 50 mL of Et_2O and 50 mL of 50% saturated aqueous KF was added. The mixture was stirred for 15 min and filtered, and the organic layer was washed with 1 × 50 mL of 50% saturated aqueous KF, 3 × 50 mL of H_2O, and 1 × 50 mL of brine. The combined aqueous layers were extracted with 25 mL of Et_2O, and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was chromatographed on 50 g of silica gel with 5% CH_2Cl_2/hexane to afford 325 mg (48%) of an orange waxy semisolid: TLC (10% CH_2Cl_2/hexane): $R_f = 0.19$; IR (film) 3060, 3004, 2929, 1637, 1481, 1441, 1375, 1209, 872, 816, 787, 757, 666, 641 cm^{-1}; UV(cyclohexane) $\lambda_{\max}(\epsilon)$ end absorption with shoulders at 207 (5400) and 232 nm (2300); ^{1}H NMR (THF-d_8, 25 °C) δ 7.09 (s, 4 H), 6.15−5.77 (m, 14 H); ^{13}C NMR (THF-d_8, 5 °C) δ 144.8, 141.5, *135.0*, 133.1, *133.0*, *132.9*, *132.4*, *132.1*, *131.9*, 130.5, 127.8. The italicized values are those for C_2-C_4 and C_6-C_8, which undergo pairwise exchange during bond shift. Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.66; H, 6.36. Attempts to reduce **3** with potassium, sodium, or lithium as described in ref 2 were unsuccessful owing to rapid decomposition of the sample.

(4) Since Karadakov et al. found that the CASSCF/6-31G*//HF/6-31G correlation energy for the D_{4h} ring inversion transition state of COT is only 3% greater than that for the D_{2d} ground state, we conclude that relative values of $\Delta E_{\mathrm{r.i.}}$ can be reliably calculated at the HF level of theory: Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Phys. Chem.* **1995**, *99*, 10186.

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