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(57) To transform an ideal TBP ground state into the ideal 30°-TR barrier configuration by single TR (ref 25), utilizing ligands O(1), O(2), O(3) as *trio*, and ligands O(4), O(5) as *pair*, and leaving equatorial ligand O(3) in the equatorial position of the new TBP, (a) contract the diequatorial angle O(2)–P–O(3) of the trio by 30° (120° → 90°); (b) tilt the pair (as a unit) 9° in the plane P, O(1), O(4), O(5), toward the apical ligand O(1) of the trio; (c) rotate (or twist) the pair against the trio in opposite directions, moving the equatorial ligand O(4) of the pair toward the equatorial ligand O(3) of the trio *that is to remain equatorial* upon completion of the permutational isomerization. These motions are assumed to be concerted; however, ab initio calculations suggest that, at least in the model PH_5, a sequential process, TBP → 0°-TR → 30°-TR, is favored (cf. ref 41).
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(64) Holmes (ref 18, 19) has suggested a correspondence between the basal bonds of the TP and the apical bonds of the TBP on the basis of "electron pair repulsion considerations".
(65) The carbon atoms of the phospholene ring, C(4), C(5), attached to the ligands, O(4), O(5) have been included with the phosphorus in plane 6 of Table IV, as well as in the corresponding planes used to calculate x in the series of compounds **7–9**. The actual value of x differs somewhat if C(4), C(5) are omitted from the plane calculations, without affecting the trend noted in the series.
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Structural Effects on the Nonradiative Decay of Alkylbenzenes. The Nature of the "α-Substitution Effect"[1]

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Abstract: The previously reported "α-substitution effect", whereby alkyl substituents on a carbon attached to the benzene ring increase nonradiative decay, is demonstrated to be caused by an increase in the rate of internal conversion ($S_0 \leftarrow S_1$ decay). Perdeuteration of the *tert*-butyl group in *tert*-butylbenzene has no effect on the phenomenon, thus eliminating involvement of the β C–H stretching mode in the decay process. However, molecules with β CH_3 groups oriented out of the plane of the benzene ring (cf. II and IV) have particularly high decay rates, and it is suggested that (1) β carbon–carbon bonds do participate in $S_0 \leftarrow S_1$ decay and (2) participation of these bonds is optimal when they are out of the plane. The ability of *tert*-butyl groups to facilitate aryl $S_0 \leftarrow S_1$ decay may be a general phenomenon.

Some time ago we reported[2] that the excited singlet lifetimes and fluorescence efficiencies of alkylbenzenes varied as a function of (at least) two structural parameters, e.g., a previously observed "xylene effect" (whereby an ortho or para arrangement of groups enhances the fluorescence efficiency (ϕ_f)) and a new "α-substitution effect" (whereby alkyl substituents on a carbon attached to the ring reduce ϕ_f). As regards the latter phenomenon, it was demonstrated that ϕ_f for monoalkylbenzenes decreases as a linear function of the number of β hydrogens; thus, *tert*-butylbenzene (nine β hydrogens) has a ϕ_f (0.032) which is 77% lower than that of toluene. In the case of *tert*-butylbenzene (and also isopropylbenzene, which has a ϕ_f 52% that of toluene), the diminution results from a sharp increase in the nonradiative decay rate (k_d). Since this rate is the sum of internal conversion (k_{ic}) and intersystem crossing (k_{isc}), a more detailed analysis of the origin of this increase necessitated the measurement of intersystem crossing efficiencies (ϕ_{isc}). These have now been determined and are reported below, together with some observations which further bear on the nature of this enhanced decay.

Experimental Section

Instrumentation. Analyses of the 2-heptene isomer compositions were performed on a Varian Aerograph 1200 vapor phase chromatograph with a Hewlett-Packard 3380A recording integrator. UV absorbance measurements were done with 1-cm cells in a Beckman DUR coupled to a Gilford 222A photometer. Alkylbenzene emission

Table I. Xenon Perturbation of Alkylbenzene (PhR) Fluorescence and *cis*-2-Heptene Isomerization[a]

R[b]	F^0/F'		Xe, mL[c]			
			6	12	16	25
Methyl	1.16	F'/F	1.28	1.68	2.43	3.09
		Y_T/Y_T'	1.24	1.45	1.65	1.86
Ethyl	1.05	F'/F	1.28	1.72	2.14	2.68
		Y_T/Y_T'	1.26	1.50	1.61	1.96
Isopropyl	1.06	F'/F	1.13	1.47	1.74	2.38
		Y_T/Y_T'	1.33	1.62	1.77	2.31
tert-Butyl	1.02	F'/F	1.01	1.07	1.20	1.34
		Y_T/Y_T'	1.58	1.99	2.71	3.68

[a] Symbols are defined in the text. [b] [Olefin] = 50 mM. [PhR]: R = methyl, 16.6 mM; ethyl, 16.8 mM; isopropyl, 17.4 mM; *tert*-butyl, 17.7 mM. [c] 1 atm.

was monitored using a previously described spectrophotofluorometer,[3] with an Oriels Optics Corp. 254-nm mercury pen lamp source through a 254 nm interference filter; data were obtained using a toluene standard.[2] Singlet lifetimes were measured on a TRW nanosecond fluorometer (Model 31A) using a deuterium lamp. Photomultiplier (RCA 1P28) output was fed into a modified Tektronix D10 single beam oscilloscope and the decay curve displayed on a Houston Instrument Omnigraphic 2000 *x*-*y* recorder.

Sample Preparation and Analytical Procedure. Five Vycor tubes, 13 × 145 mm, with necks having graded Vycor to Pyrex seals, were charged with 5 mL of cyclopentane stock solution, 50 mM in *cis*-2-heptene, with sufficient alkylbenzene to provide an absorbance of 2.5 cm^{-1} at 254 nm. Rigorous degassing was effected with four freeze-pump-thaw cycles at $<1 \times 10^{-4}$ Torr. Xenon was distilled into the tubes in a manner similar to that of Carroll and Quina.[4] The xenon cylinder was connected to the vacuum line by a glass manifold, sections of which could be isolated for delivery of a graded series of volumes (6, 12, 16, and 25 mL, filled to 1 atm) into four of the tubes. All five tubes were then sealed. Relative fluorescence emission was determined, and the tubes were then suspended in a Rayonet RPR-100 reactor by means of an MGR-100 merry-go-round apparatus and irradiated with a single lamp emitting light in the 2537-Å region. Irradiations were carried out to low (<5%) levels of olefin isomerization in all cases save that of *tert*-butylbenzene, where isomerization did not exceed 7%. All isomerization data were corrected for back reaction. Analyses for *trans*-2-heptene were performed using a 20 ft × 0.25 in. β,β'-oxydipropionitrile column at 0 °C. Correction for singlet quenching (F^0/F') was made for each alkylbenzene in a separate series of experiments. For each compound, two tubes were prepared containing cyclopentane solutions of the substrate at the working concentration used in the perturbation experiment, with one of the solutions 50 mM in olefin. All tubes were degassed and sealed, and the relative fluorescence emissions determined. The relative values of ϕ_{isom} (Y_T/Y_T') and fluorescence intensity (F'/F) were then treated as described.[4]

Chemicals. Cyclopentane (Burdick and Jackson, "distilled in glass") was used as received. Ethylbenzene (MCB reagent), isopropylbenzene (MCB), and *tert*-butylbenzene (ChemSampCo) were purified by preparative VPC on a 10 ft × 0.25 in. column of 10% SE-30 on Gas-Pack W followed by short path distillation. Toluene (Mallinckrodt reagent) and 1-phenyldecane (Aldrich) were sufficiently pure by GLC analysis on the above column that these reagents were distilled directly. *cis*-2-Heptene (K & K Laboratories) was purified using a 10 ft × 0.375 in. 30% $AgNO_3$-ethylene glycol column prior to distillation. Analyses of the unirradiated olefin for the trans isomer were performed as described below; the amount of trans isomer never exceeded 0.21%. Xenon (Matheson research grade) was used as received.

(*tert*-Butyl-d_9)benzene (I). This compound was prepared by the method of Nightingale and co-workers[5] from 2-chloro-2-methylpropane-d_9 (Aldrich) and anhydrous ferric chloride (Fisher) in benzene. The (*tert*-butyl-d_9)benzene so obtained is a colorless liquid: bp 68-69 °C (20 mm); IR (neat) 3.31, 4.52, 6.28, 6.76, 6.99, 9.51, 9.90, 13.16, 13.66, and 14.45 μ; NMR ($CDCl_3$) δ 7.34; mass spectrum *m/e* (rel intensity) 143 (29), 126 (12), 125 (100), 124 (13), 94 (18), 93 (34), and 46 (14) (>99% d_9). Anal. Calcd for $C_{10}H_5D_9$: C, 83.82; H, 3.52; D, 12.66. Found: C, 84.09; H, 3.49; D, 12.60.

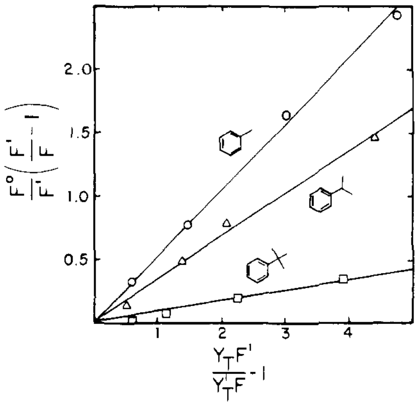


Figure 1. Representative least-squares plots for toluene (○), isopropylbenzene (△), and *tert*-butylbenzene (□) (see Tables I and II).

1,3-Dimethyl-2-isopropenylbenzene. 2,6-Dimethylbenzoic acid (10 g, 66 mmol) (Aldrich) was treated with trimethylaluminum (26 mL, 266 mmol) (Texas Alkyls) according to the method of Meisters and Mole.[6] After 36 h at 135-150 °C, workup of the hydrolyzed reaction mixture afforded 7 g of a pale yellow oil. Chromatography on alumina (Merck) with hexane afforded 1.9 g (19%) of the crude product. Purification on a Carbowax 20M column provided pure material: IR (neat) 6.09, 6.85, 6.98, 7.30, 7.35, 9.31, 11.17, and 13.08 μ; NMR ($CDCl_3$) δ 7.03 (3 H, s), 5.25 (1 H, m), 4.75 (1 H, m), 2.23 (6 H, s), and 1.94 (3 H, m); mass spectrum *m/e* (rel intensity) 146 (82), 131 (100). Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.28; H, 9.65.

1,3-Dimethyl-2-isopropylbenzene (II). 1,3-Dimethyl-2-isopropenylbenzene (500 mg, 3.42 mmol) was dissolved in ethyl acetate (50 mL) and hydrogenated using 150 mg of 10% palladium on charcoal catalyst. After filtration of the catalyst and removal of the solvent, the product was purified on a Carbowax 20M column to give 423 mg (84%): IR (neat) 6.85, 7.28, 7.39, 9.46, and 13.11 μ; NMR ($CDCl_3$) δ 1.31 (6 H, d, J = 8 Hz), 2.35 (6 H, s), 3.41 (1 H, septet, J = 8 Hz), and 6.96 (3 H, s); mass spectrum *m/e* (rel intensity) 148 (23), 133 (100). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.94; H, 10.89.

(1-Methylcyclohexyl)benzene (IV). Alkylation of benzene with 1-methylcyclohexanol (Aldrich) in sulfuric acid was carried out by the method of Sidorova[7] to afford IV in 31% yield as a colorless liquid, bp 132-135 °C (17 mm) (lit.[7] 136-137 °C (34 mm)).

Results and Discussion

The recently detailed xenon perturbation method of Carroll and Quina[4] was used to determine ϕ_{isc} values. This method involves the measurement of alkylbenzene fluorescence with and without xenon, and the degree of sensitized olefin isomerization, also with and without xenon. Data, corrected for back reaction, are presented in Table I, wherein (1) F^0, F', and F are the relative fluorescence intensities with (a) no olefin or xenon, (b) olefin but no xenon, and (c) olefin plus xenon, respectively; (2) Y_T and Y_T' are the yields of olefin geometric isomer with and without xenon, respectively. The data in Table I, when plotted (see Figure 1) as

$$\left(\frac{F^0}{F'}\right)\left(\frac{F'}{F}-1\right)=\phi_{isc}\left(\frac{Y_T}{Y_T'}\frac{F'}{F}-1\right)$$

provide ϕ_{isc} as the slope; these efficiencies, when combined with previously measured[2] singlet lifetimes, allow for a complete description of the photophysical properties of these compounds (Table II). It now becomes clear that ϕ_{isc} is reduced, within this series, in like fashion to ϕ_f, and that *the previously reported enhanced nonradiative decay which culminates in tert-butylbenzene*[2] *is specifically the consequence of increased internal conversion.*

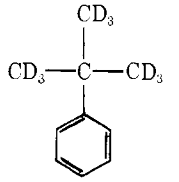
This having been demonstrated, we concerned ourselves with the origin of the high k_{ic} which characterizes *tert*-butylbenzene. There has been considerable discussion in the literature

Table II. Photophysical Properties of Some Alkylbenzenes (PhR)

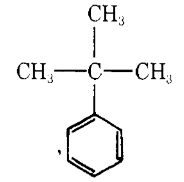
R	ϕ_f[a]	ϕ_{isc}[b]	τ_f,[c] ns	k_f, 10^6 s^{-1}	k_{ic}, 10^6 s^{-1}	k_{isc}, 10^6 s^{-1}
Methyl	0.14	0.52 ± 0.01 (0.51)[d]	35.2	4.0	9.6	15.
Ethyl	0.11	0.44 ± 0.02	35.1	3.1	13.	13.
Isopropyl	0.073	0.34 ± 0.01	24.5	3.1	24.	14.
tert-Butyl	0.032	0.086 ± 0.007	10.0	3.2	88.	8.6

[a] Reference 2. [b] This work, Table I; errors are standard deviations from a least-squares treatment. [c] Reference 2; we estimate the *maximum* error for these data to be ±1 ns. [d] Reference 4.

of the possible involvement of toluene's α C-H vibrational modes in radiationless decay from the *triplet* state. Though a recent report minimizes this involvement,[8] the empirical correlation we observed[2] between ϕ_f and the number of β hydrogens led us to synthesize (*tert*-butyl-d_9)benzene (I). *The*



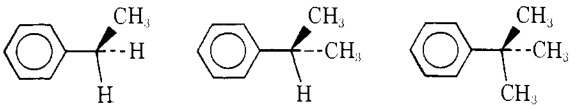
I

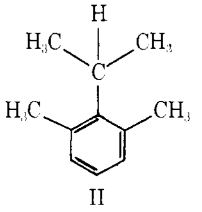


	I	
ϕ_f	0.031	0.032
$^1\tau$, ns	10.	10.

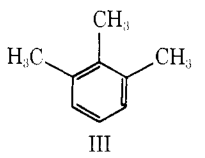
ϕ_fs and $^1\tau$s for perdeuterated vs. nondeuterated material are within experimental error and confirm that, despite the correlation mentioned above, the β C-H stretch is not coupled into the $S_0 \leftarrow S_1$ decay.

We therefore considered that the α, β C-C bonds of the branched alkyl side chain in some way promote aryl internal conversion. When we noted that the increase in k_{ic}, for the series ethyl-, isopropyl-, and *tert*-butylbenzene, mirrors a progressively increasing preference for the out-of-plane conformations shown below,[9,10] we theorized that not only might the α,β C-C bonds be involved, but that a stereoelectronic requirement may be present as well. To test this hypothesis, we synthesized compounds II and IV, and compared them with appropriate models (III and V, respectively); the data are shown below the structures.

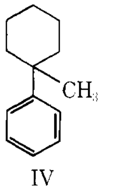




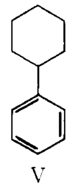
II



III



IV

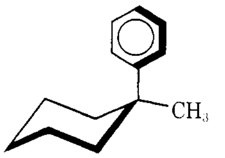


V

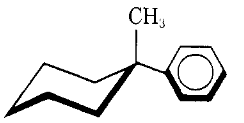
	II	III	IV	V
ϕ_f	0.0078	0.081	0.021	0.089
$^1\tau$, ns	5.8	35 (ref 4b)	8.1	29.2 (ref 2)
k_d, 10^6 s^{-1}	170	26	120	31

Compound II was chosen because the steric constraints of the 2,5-dimethyl groups should lock the isopropyl group into a conformation in which α C-CH$_3$ bonds are fixed out of the plane of the ring.[11] The consequence for k_d is indeed dramatic; its sixfold increase, relative to that of III, may be compared to the factor of 1.5 for isopropylbenzene relative to toluene. In fact, II has one of the shortest lived excited singlet states we have measured for an alkylbenzene.

Compound IV was chosen because calculations[12] indicate that IVa and IVb are its preferred conformations (IVa being of lower energy). Both IVa and IVb are estimated to be several kilocalories/mole lower in energy than conformers having the methyl in the plane of the benzene ring. Again, the fourfold increase in k_d of IV relative to V may be compared with the factor of 2.5 for *tert*-butylbenzene relative to isopropylbenzene. *We believe that the data for II and IV provide additional evidence for the importance of α,β C-C bonds in the nonradiative decay process, and support the hypothesis that these bonds are most effective when out of the plane of the ring.*[13]

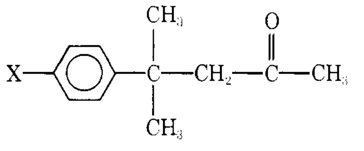


IVa



IVb

There are indications that the effect of a *tert*-butyl group on nonradiative decay may be fairly general. Thus, the singlet lifetime of VIa is a factor of 10 less than that of VIb[14] (*p*-xylene and toluene have comparable $^1\tau$s).[2] Even in a more complex molecule such as indigo, insertion of *tert*-butyl groups has been observed to lower ϕ_f and $^1\tau$.[15] The detailed mechanism by which C-C bonds accelerate aryl $S_0 \leftarrow S_1$ decay remains to be elucidated.[16]



VIa, X = *t*-Bu
b, X = H

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(16) It is worth noting that at 77 K in an isopentane glass, the ϕ_f for *tert*-butylbenzene increases somewhat, relative to toluene, but is still low (58% of toluene). It is also interesting that α-methylation of acetone *decreases* nonradiative rates; cf. D. A. Hansen and E. K. C. Lee, *J. Chem. Phys.*, **62**, 183 (1975).

The Structure of 1,3,6,8-Tetra-*tert*-butylnaphthalene

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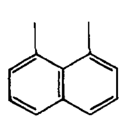
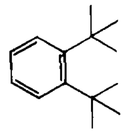
Abstract: The detailed molecular structure of a *peri*-di-*tert*-butylnaphthalene has been determined by x-ray crystallography and molecular mechanics calculation. Both methods describe a highly distorted nonplanar framework, a result which serves to confirm previous structural assumptions that were based on other spectroscopic techniques.

Highly congested molecules always present challenges to chemists. There is the synthesists' problem of trying to prepare such molecules and there is the theoreticians' goal of trying to predict or interpret why the structures and properties come out the way they do. Both the 1,8-dimethylnaphthalene **1** and the *o*-di-*tert*-butylbenzene system **2** have been subjects of molecular mechanics calculations and x-ray crystallography.[2,3] In both molecules, the methyl groups are closer than permitted by the sum of van der Waals radii and hence the molecules are strained. In both systems, the adjustment to the strain was observed experimentally as an outward in-plane bending of substituent groups. The major adjustment of the aromatic ring was bond angle deformation, but there was no significant deviation from planarity. When the methyl groups of 1,8-dimethylnaphthalene are replaced with *tert*-butyl groups, the congestion is much more severe. The successful synthesis of such compounds[4] was an invitation to molecular mechanics methodology[3b,5] to determine the structure of the system, particularly since the x-ray crystallographic study had not been completed when the calculations were done. Now that the x-ray work has been concluded, we wish to report both the calculated and experimental structures of the 1,8-*peri*-*tert*-butylnaphthalene system, specifically, the tetra-*tert*-butylnaphthalene **3**.



1



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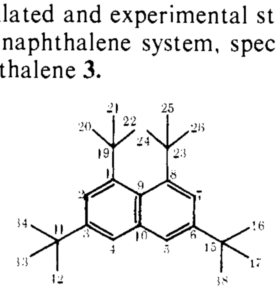

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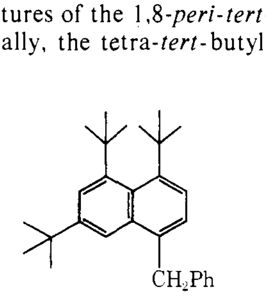

4

Experimental Section

X-Ray Analysis. The crystals are triclinic with $a = 9.886\ (3)$, $b = 10.437\ (3)$, $c = 12.125\ (4)$ Å, $\alpha = 82.48\ (3)$, $\beta = 85.63\ (3)$, $\gamma = 71.32\ (3)°$, $V = 1170$ Å^3. The space group is $P\bar{1}$ with two molecules per cell, $D_c = 0.999$ g cm^{-3}, μ (Cu Kα radiation) = 4.11 cm^{-1}.

Intensity data were collected on an Enraf-Nonius CAD 4 diffractometer, using monochromatized Cu Kα radiation, up to a limit of $\theta = 75°$. The $\omega - 2\theta$ scanning mode was used and reflections were accepted as observed on the criterion $I/\sigma I > 3$. Complete data were collected from two separate crystals, a small one approximately cube shaped with edge 0.2 mm, and a much larger crystal, roughly spherical and with mean diameter 0.67 mm. A total of 4452 independent reflections, or 89% of those possible, was accepted. Initial work was done using the large crystal data, but after structure solution and isotropic refinement, the two sets were combined by a least-squares fit of the scales, at the same time subtracting out the differential spherical absorption between the two crystals. Some extinction was evident in the low angle data from the large crystal. Therefore data from the small crystal only were used for the range $\sin \theta/\lambda < 0.325$ Å^{-1}. This reduced the data to 4027 reflections giving a data/parameter ratio of 10.2 in the final refinement. Data reduction was carried out via NRC program 02.[6]

The E statistics favored a centrosymmetric structure and this was strengthened by the results of the ORNL search program ORTRAN.[7] A 12-atom moiety consisting of the naphthalene ring and the two presumably coplanar first substituent atoms in the 3,6 positions was used and only one independent orientation was found. In order to determine the translation, this fragment was placed in an arbitrary position of the space group $P1$ and atoms added in from successive electron density maps (NRC program 08[8]) until this molecule was complete. The second molecule then appeared related by a center of symmetry to the first. Coordinates were then transformed to this center as origin and refinement carried out in the space group $P\bar{1}$. Full-matrix least-squares refinement of the carbon atom parameters was carried out on a CDC 6600 computer using the ORNL program ORXFLS3.[9] Two cycles with isotropic thermal parameters reduced R to 0.158, and two subsequent cycles using anisotropic thermal parameters gave an R of 0.096. The hydrogen atoms were then located using a modified FORDAP (BNL)[10] program. Subsequent refinement (anisotropic carbon atoms, isotropic hydrogen atoms) gave a final R value 0.057 and wR of 0.058 for all observed reflections. The weighting scheme used was based on the counting statistics and the function minimized in least-squares refinement was $\Sigma w(F_o - KF_c)^2$. The form factors used are those given in the International Tables.[11] The observed and calculated structure factors are found in Table I (microfilm edition). The structural parameters for all atoms are given in Table II. Bond distances and bond angles are found in Table III.

Molecular Mechanics Calculations. The conclusions here were arrived at simultaneously with and independently from the x-ray work. The previously described force field (MMPI-1973) was used.[3b,5]

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