compound. The quaternary benzenoid carbons attached to the bridgehead carbons were composed of seven lines with the intensity ratios of 4:2:2:2:2:4:2. Inspection of molecular models reveals that the middle triptycene unit has local C_2 symmetry with the C_2 axis lying in the plane of one (a) of the benzene rings as above. Thus ring a is diastereotopic to the other two (b and c rings). Rings b and c are equivalent in such a way that the upper carbons in ring b are equivalent to the bottom ones in ring c and vice versa. As a result, the quaternary benzenoid carbons of the unsubstituted triptycene unit show a 2:2:2 triplet in the ^{13}C spectrum.

Interconversion between the meso and racemic compounds of **1** takes place at higher temperatures as a result of the gear slippage process. The rates of isomerization from the *dl* to meso compounds were measured in diphenylmethane solutions in the temperature range 238–332 °C to give the activation energy parameters as follows: $\Delta H^{\ddagger} = 42.1 \pm 1.3$ kcal/mol, $\Delta S^{\ddagger} = -3.2 \pm 2.3$ eu, $E_a = 43.2 \pm 1.3$ kcal/mol, $\log A = 12.8 \pm 0.5$, and K (*dl*/meso) = 2.05 ± 0.07. These values are within the experimental errors the same as those obtained for **2** except that A is about twice as much in **1**, supporting the same gear slippage processes participating in **1** and **2**.

Previously we reported that the recognition of the conformational relationship between the two CMe_2CN substituents was possible across the bridgeheads of a triptycene nucleus since torsion of the pivot bonds was fully restricted as in **4**.[6] The present results extend the stereochemical notion in that the two substituents may rotate rapidly in the geared motion[7] and suggest that transfer of information from one end of the molecule to the other end could take place in large molecules via cooperativity of the torsional motions of the chain.

Registry No. (*dl*)-**1**, 86456-44-2; *meso*-**1**, 86456-45-3; 9-bromo-3-chlorotriptycene, 78129-59-6; bis(peroxy ester), 86456-46-4; triptycene-9,10-dicarbonyl dichloride, 21896-62-8.

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[7] In **1**, conformation of the molecular skeleton is not necessarily fixed as shown in **3**, but additional conformers **3a–c** are also conceivable. None equivalence of the unsubstituted benzene rings in the middle triptycene unit will be more readily understood if the molecules are assumed to have the conformation frozen as in **3c**.

Photoinitiated Chain Decomposition of Phenyl Isocyanate via Its Reaction with Phenylnitrene

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The photoinitiated autocatalytic chain decomposition (PACD) of phenyl azide is observed by measurement of quantum yields of disappearance ($\phi(-PhN_3)$) greater than unit efficiency.[1] Azobenzene[2] is formed exlusively as the E isomer[3] via either the dimerization of phenylnitrene[4] (eq 2), formed upon irradiation of phenyl azide[5-9] (eq 1), or the reaction of phenylnitrene with phenyl azide at N_1 (eq 3) to afford 1,2-diphenyltetraazadiene (**1**),

$$PhN_3 \xrightarrow{h\nu} PhN + N_2 \qquad (1)$$

$$2PhN \rightarrow PhN{=}NPh \qquad (2)$$

$$PhN + PhN_3 \rightarrow \underset{\mathbf{1}}{[Ph\overset{+}{N}(N{=}\overset{-}{N}){=}NPh]} \rightarrow PhN{=}NPh + N_2 \qquad (3)$$

which readily decomposes into azobenzene and molecular nitrogen. Nitrene reaction at N_3 could afford 1,4-diphenyltetraazadiene (**2**), which is thought to decompose into nitrogen and *two* phenyl nitrenes (eq 4). Alternatively, the reaction of phenyl nitrene with

$$PhN + PhN_3 \rightarrow PhN{=}\underset{\mathbf{2}}{NN}{=}NPh \rightarrow 2PhN + N_2 \qquad (4)$$

phenyl azide may directly afford nitrogen and *two* phenylnitrenes (eq 5). Reactions 4 or 5 would then serve as the chain propagation step.

$$PhN + PhN_3 \rightarrow 2PhN + N_2 \qquad (5)$$

To distinguish between these autocatalytic chain steps, we have generated phenylnitrene via an alternate route that precludes formation of 1,4-diphenyltetraazadiene. Since the isocyanate group ($N{=}C{=}O$) is isoelectronic with the azide group ($N{=}N^+{=}N^-$), phenyl isocyanate (PhNCO) was selected for study. Photolysis of phenyl isocyanate in the vapor phase[10] or in organic matrices[11] affords phenylnitrene. Nitrene formation also may have occurred upon irradiation of 2-biphenyl isocyanate[12] or alkyl isocyanates.[13] Thus, we have made a quantitative photochemical investigation of phenyl isocyanate.

Phenyl azide, prepared according to literature procedures,[14] was vacuum distilled prior to use. 3-Methylpentane (99+%, Phillips Petroleum) was distilled from Dri-Na (Baker) prior to use as the solvent for all low-temperature experiments. Acetonitrile (UV, Burdick and Jackson) and phenyl isocyanate (puriss, p. a., Fluka) were used directly. Electronic absorption spectra were recorded at 77 K on a Perkin-Elmer 330 spectrophotometer equipped with a Data Station. Long-stemmed, flat-faced 10 × 10 mm Suprasil quartz cells (Worden Quartz) and a double-jacketted, liquid-nitrogen quartz Dewar with flat-faced, Suprasil windows (Worden Quartz) were used. Room-temperature spectra were recorded on a Perkin-Elmer 575 spectrophotometer with quartz cuvettes (Precision Cells). A 1000-W Hg–Xe lamp and Schoeffel GM-252 $^1/_4$ m monochromator was used to isolate 227-nm radiation. Unfiltered light from a 450-W Hg lamp was also used. Quantum yields of disappearance of phenyl isocyanate ($\phi(-PhNCO)$) were determined at room temperature by measuring the decrease in absorbance of phenyl isocyanate upon 227-nm irradiation, while an isosbestic point (236 nm in acetonitrile) was maintained. $\phi(-PhNCO)$ for solutions > ca. 10^{-3} M were similarly determined, but after quantitative dilutions. The light flux was calibrated using potassium ferrioxalate.[15] Photoproducts were separated by high-pressure liquid chromatography (LC) by using a Waters ALC/GPC 204 LC, Waters μPorasil column (12 × 0.25 in.), 2% anhydrous ether in hexane, ca. 2 mL/min flow rate, 1500 psi, and 280-nm absorbance detection and characterized by high-pressure LC retention-time and absorption spectral data.

Irradiation of 10^{-2}–10^{-4} M phenyl azide in 3-methylpentane at 77 K results in a decrease in intensity of the 250-nm absorption maximum and appearance of a bathochromic absorption. An isosbestic point at 288 nm and higher energy bands at 237 and 242 nm are also observed. Irradiation of 10^{-2}–10^{-4} M phenyl

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Table I. Quantum Yields of Disappearance of Phenyl Isocyanate upon 227-nm Irradiation at Room Temperature

	$\phi(-\text{PhNCO})^b$		
concn, M[a]	Ar[20]	O_2[20]	tetracyanoethene, 10^{-2} M
10^{-2}	7.8	2.8	2.1
10^{-3}	0.35	0.25	
10^{-4}	0.090	0.075	
10^{-5}	0.072	0.057	

[a] Acetonitrile; exact concentrations vary from (1.01 to 1.74) × 10^{-x} M, where x = 2, 3, 4, or 5. [b] $\phi(-\text{PhNCO}) \pm 20\%$; average of several trials.

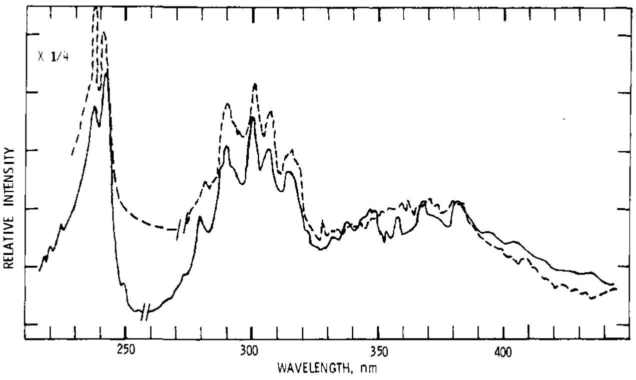

Figure 1. True absorption spectra[16] of phenylnitrene[17] obtained upon irradiation of 8.55×10^{-5} M phenyl azide (—) and 2.56×10^{-4} M phenyl isocyanate (- - -) in 3-methylpentane at 77 K.

isocyanate in 3-methylpentane at 77 K results in a decrease of phenyl isocyanate absorption and concommitant appearance of bathochromic absorptions. True absorption spectra[16] of the intermediates formed upon irradiation of phenyl azide and of phenyl isocyanate at 77 K are essentially indentical (Figure 1) and are similar to that reported by Reiser et al.[6] and by Smirnov and Brichkin.[9] Hence, phenyl nitrene[17] is formed upon irradiation of phenyl isocyanate.[10,11]

Irradiation of a room-temperature, aerated 10^{-4} M solution of phenyl isocyanate in 3-methylpentane with 227-nm light results in the formation of *E*-azobenzene and nitrosobenzene, $\phi(-\text{PhNCO}) = 0.15$. However, at $[\text{PhNCO}] = 2 \times 10^{-2}$ M in deaerated 3-methylpentane,[20] $\phi(-\text{PhNCO}) = 12.2$; a value greater than unit efficiency which is indicative of a chain decomposition reaction of phenyl isocyanate. *E*-azobenzene is the only photoproduct. Upon irradiation of phenyl isocyanate in acetonitrile similar results are observed. Specifically, at ca. 2×10^{-5} M, $\phi(-\text{PhNCO}) = 0.072$, but is notably higher at higher [PhNCO] and decreases upon oxygen-saturation[20] or upon addition of an equimolar concentration of tetracyanoethene. Table I is a summary. Nitrosobenzene is a primary photoproduct when phenyl isocyanate is irradiated in oxygen-saturated solution, a reaction product also obtained for phenyl azide.[3]

The concentration dependence of $\phi(-\text{PhNCO})$ parallels that of $\phi(-\text{PhN}_3)$ determined for phenyl azide[1] and can be understood if a chain decomposition reaction were also occurring upon irradiation of phenyl isocyanate. Irradiation of phenyl isocyanate results in phenylnitrene formation[10,11] (eq 6), which can dimerize

$$\text{PhNCO} \xrightarrow{h\nu} \text{PhN} + \text{CO} \qquad (6)$$

to form azobenzene (eq 2) or propagate the chain by reaction with phenyl isocyanate to form (a) carbon monoxide and *two* phenylnitrenes (eq 7), (b) the substituted cyclic species 2,3-diphenyldiaziridinone (**3**), or (c) 2-phenyloxaziridine (**4**) (eq 8).

$$\text{PhN} + \text{PhNCO} \rightarrow 2\text{PhN} + \text{CO} \qquad (7)$$

$$\text{PhN} + \text{PhNCO} \rightarrow \underset{\mathbf{3}}{\text{Ph}\overline{\text{NN(Ph)C}}{=}\text{O}} + \underset{\mathbf{4}}{\text{Ph}\overline{\text{NC(O)}}{=}\text{NPh}} \qquad (8)$$

2,3-Dialkyldiaziridinones have been synthesized[21-23] and afford azoalkanes upon thermolysis.[22] A nitrenoid fragment may be formed during the reaction.[23] 2-Phenyloxaziridines afford phenylnitrene upon photolysis.[24]

Were analogous reactions to occur upon reaction of phenylnitrene with phenyl azide, triaza species would be expected via insertion at N_1–N_2 (**5**, eq 9) or N_2–N_3 (**6**, eq 10). If formed,

$$\text{PhN} + \text{PhN}_3 \rightarrow \underset{\mathbf{5}}{\text{Ph}\overline{\text{NN}^{+}\text{(N}}\text{Ph}){=}\text{N}^{-}} \rightarrow \text{PhN}{=}\text{NPh} + \text{N}_2 \qquad (9)$$

$$\text{PhN} + \text{PhN}_3 \rightarrow \underset{\mathbf{6}}{\text{Ph}\overline{\text{N}^{-}\text{N}^{+}}{=}\text{NNPh}} \rightarrow 2\text{PhN} + \text{N}_2 \qquad (10)$$

6 would have to decompose into *two* phenyl nitrenes to propagate the chain reaction, while **5** is expected to yield azobenzene and thus terminate the chain reaction. Experimental evidence for the existence of a triaza species can be derived from the photochemical cyclization of an azimine to a triaziridine[25] and from the reaction of ^{15}N-enriched hydrazine with nitrous acid, which may have formed a cyclic intermediate.[26]

The number of propagation steps (n) in the autocatalytic chain decomposition can be estimated from $2^n = \phi/\phi_0$ where $\phi_0 = \phi(-\text{PhNCO})$ at infinite dilution (approximated using $\phi = 0.057$ at $[\text{PhNCO}] = 10^{-5}$ M). For $\phi(-\text{PhNCO}) = 9.3$ at $[\text{PhNCO}] = 1.5 \times 10^{-2}$ M, $n = 7.35$. This compares to $n = 9.2$ and 6.7 for phenyl azide at $[\text{PhN}_3] = 3 \times 10^{-2}$ and 3×10^{-3} M, respectively.[1,27] Since (a) the magnitudes of n are the same, (b) a 1,4-diphenyltetraazadiene intermediate is not possible for a phenylnitrene–phenyl isocyanate reaction, and (c) nanosecond transient absorption spectral studies of phenyl azide and of phenyl isocyanate have afforded identical spectra,[28] it is conceivable that no intermediate exists for the phenylnitrene–phenyl azide reaction. The chain propagation reactions would result from a phenylnitrene sensitized decomposition of phenyl azide (eq 5) or phenyl isocyanate (eq 7) to form *two* phenylnitrenes.

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Registry No. Phenyl isocyanate, 103-71-9; phenylnitrene, 2655-25-6; (*E*)-phenyl azide, 17082-12-1.

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(16) The true absorption spectra of the intermediates were obtained by subtraction of the absorption spectra obtained prior to irradiation, adjusted for the fraction of starting material remaining after irradiation, from the absorption spectra recorded after irradiation.

(17) We have not yet attempted to address the question of whether phenylnitrene undergoes intramolecular rearrangement to form 7-azabicyclo[4.1.0]hepta-2,4,6-triene[18] or 1-aza-1,2,4,6-cycloheptatetraene.[19]

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