Recognition of the Phase Relationship between Remote Substituents in 9,10-Bis(3-chloro-9-triptycyloxy)triptycene Molecules Undergoing Rapid Internal Rotation Cooperatively

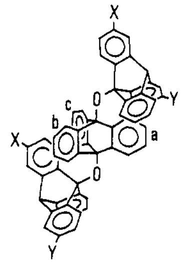
Noboru Koga, Yuzo Kawada, and Hiizu Iwamura*

Department of Applied Molecular Science
Institute for Molecular Science
Okazaki 444, Japan

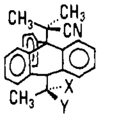
Received March 16, 1983

The torsional motions around the two C–X bonds at the bridgehead of the (9-triptycyl)$_2$X molecules are rapid and take place in strictly coupled disrotation. As a result, a certain phase relationship is established between the appropriately labeled teeth on the different wheels of the cogwheeling molecular bevel gear, and a new concept of stereoisomerism with respect to the phase between the labeled teeth has been introduced therefrom.[1,2] Labeling of one benzene ring on each triptycene unit, for example, gave the meso and racemic compounds. By bridging two triptycene units that have three different benzene rings, a meso and four *dl* pairs were obtained as predicted by the theory.[1f] We would like to report that the phase relationship between the labels can be recognized even when the two wheels are separated by the bridgeheads of an additional triptycene framework. This has now been demonstrated by the preparation of the doubly geared molecules **1**, separation of the meso and racemic compounds by means of HPLC, and characterization of the isomers by high-resolution ^{13}C NMR spectra. The results are surprising in view of the fact that the molecular framework is so flexible and contains very many possible conformers. The macroscopic properties are considered to be dictated by the average of the corresponding properties of each conformer and therefore expected not to differ too much.

The synthetic strategy employed here is in principle the same as that used for the preparation of bis(9-triptycyl) ethers.[1] A diethyl ether solution of the lithium salt of 3-chloro-9-hydroperoxytriptycene was obtained by the reaction of 9-bromo-3-chlorotriptycene[1d] with butyllithium followed by reaction with oxygen in ether at −77 °C and allowed to react with triptycene-9,10-dicarbonyl dichloride to give the bis(peroxy ester), mp 110–160 °C dec, in 10% yield.[3] Thermal decomposition in perfluorodecalin at 150 °C gave diether **1** in 32% yield as white powder. The product was subjected to HPLC on microsilica with 4% CH$_2$Cl$_2$ in hexane elution.[4] In Figure 1 is given a typical chromatogram that shows that the first fraction was the statistically more abundant racemic isomer, and the second more polar fraction was the less abundant meso isomer. The isomers of the corresponding monoether, bis(3-chloro-9-triptycyl) ether (**2**), showed the opposite chromatographic behavior under similar conditions.[1d]



1, meso, X = Cl; Y = H
1, *d* or *l*, X = H; Y = Cl
3, X = Y = H



4, meso, X = CH$_3$; Y = CN
4, *d* or *l*, X = CN; Y = CH$_3$

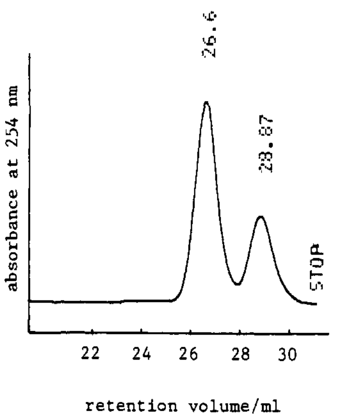
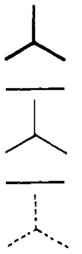
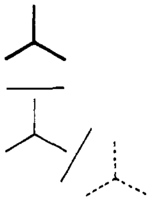


Figure 1. Analytical HPLC separation of the racemic (fraction 1) and meso (fraction 2) diether **1**.

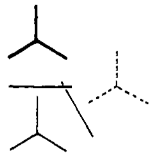
^{13}C NMR spectra obtained at 100.40 MHz were instrumental in verifying the structural assignment.[5] The unsubstituted diether **3**, showed six tertiary and three quaternary aromatic carbon signals, demonstrating the presence of only one kind of the benzene ring each for the inner and outer triptycene units. The observation also confirmed the rapid internal rotation around the C–O bonds in these molecules in the NMR time scale. The second fraction, mp 505 °C, from the HPLC of **1** gave a simpler ^{13}C NMR spectrum than the first fraction and therefore should be assigned to the more highly symmetric meso isomer. We had naively thought that the three benzene rings in the middle triptycene unit would be equivalent. This should have given the quaternary ring carbons attached to the bridgehead carbons as a quintet in 6:4:4:2:2 intensity ratios. The spectrum obtained showed six lines in 4:4:4:2:2:2 ratios instead. Comparison with the ^{13}C NMR spectra of isomeric **2** and of **3** revealed that the signal corresponding to the apparently equivalent six quaternary ring carbons of the middle triptycene moiety was now split into a 4:2 doublet with no more than 0.1-ppm spacing. It has been shown by a careful study of the conformation that the molecule of the meso isomer belongs effectively to the C_{2v} point group with the C_2 axis lying in the plane of one (a) of the benzene rings and passing through the center of the middle triptycene unit. Therefore, the other two benzene rings (b and c) are equivalent while ring a is unique in that it never comes next to the labeled rings of the outer triptycene units. Thus the assignment of the meso isomer was justified.



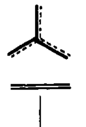
3



3a



3b



3c

The first fraction of the HPLC of **1**, mp 509 °C, showing a more complicated ^{13}C NMR spectrum, should be the racemic

---

[1] (a) Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547. (b) Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1981**, *103*, 958. (c) Kawada, Y.; Iwamura, H. *Tetrahedron Lett.* **1981**, *22*, 1533. (d) Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1983**, *105*, 1449. (e) Kawada, Y.; Iwamura, H.; Okamoto, Y.; Yuki, H. *Tetrahedron Lett.* **1983**, *24*, 791. (f) Kawada, Y.; Iwamura, H.; Okamoto, Y. *Ibid.*, submitted for publication.

[2] (a) Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961. (b) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957. (c) Johnson, C. A.; Guenzi, A.; Mislow, K. *Ibid.* **1981**, *103*, 6240. (d) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *Ibid.* **1983**, *105*, 1427. (e) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *Ibid.* **1983**, *105*, 1438.

[3] New compounds in this paper gave satisfactory analytical and ^{1}H and ^{13}C NMR data. Melting points were examined by the DSC technique on a Du Pont 990 thermal analyzer. Bis(peroxy ester) showed only an exothermic curve, while both isomers of **1** gave a sharp endothermic peak followed by a broad exothermic curve.

[4] HPLC was performed on a Waters Model ALC/GPC 244 system. The analytical and preparative runs were carried out on $^1/_2$ in. × 1 ft and $^3/_8$ in. × 1 ft μPorasil columns with the flow rates of 1 and 6 mL/min, respectively.

[5] Obtained on a JEOL GX-400 spectrometer.

0002-7863/83/1505-5498$01.50/0

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.

---

(6) Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1973**, 232.

(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

Walter H. Waddell* and Natalie B. Feilchenfeld

Department of Chemistry
and Center for the Joining of Materials
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Received January 10, 1983

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

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

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

---

* Present address: The Goodyear Tire and Rubber Company, Akron, OH.

(1) Waddell, W. H.; Lee Go, C. *J. Am. Chem. Soc.* **1982**, *104*, 5804.

(2) Horner, L.; Christmann, A.; Gross, A. *Chem. Ber.* **1963**, *96*, 399.

(3) Lee Go, C.; Waddell, W. H. *J. Org. Chem.*, in press.

(4) Smith, P. A. S. In "Nitrenes"; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970; p 99.

(5) Reiser, A.; Fraser, V. *Nature (London)* **1965**, *208*, 682.

(6) Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162.

(7) Reiser, A.; Wagner, H. M.; Marley, R.; Bowes, G. *Trans. Faraday Soc.* **1967**, *63*, 2423.

(8) Reiser, A.; Willets, F. N.; Terry, G. C.; Williams, V.; Marley, R. *Trans. Faraday Soc.* **1968**, *64*, 3265.

(9) Smirnov, V. A.; Brichkin, S. B. *Chem. Phys Lett.* **1982**, *87*, 548.

(10) Porter, G.; Ward, F. R. S.; Ward, B. *Proc. R. Soc. London, Ser. A* **1968**, *303*, 139.

(11) Kuck, V. J.; Wasserman, E.; Yager, W. A. *J. Phys. Chem.* **1972**, *76*, 3570.

(12) Swenton, J. C. *Tetrahedron Lett.* **1967**, 2855.

(13) Bamford, D. A.; Bamford. C. H. *J. Chem. Soc.* **1941**, 30. Boyer, J. H.; Krueger, W. E.; Mikol, G. J. *J. Am. Chem. Soc.* **1967**, *89*, 5504. Mikol, G. J.; Boyer, J. H. *J. Chem. Soc., Chem. Commun.* **1972**, *439*. Boyer, J. H.: Mikol, G. J. *J. Heterocycl. Chem.* **1972**, *9*, 1325.

(14) Lindsay, R. O.; Allen, C. F. H. *Org. Synth.* **1955**, *3*, 710.

(15) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966.

0002-7863/83/1505-5499$01.50/0