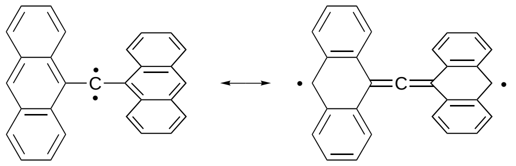
[10] T. Mizuno, M. Takeuchi, S. Shinkai, *Tetrahedron* **1999**, *55*, 9455–9468.
[11] In general, Lewis acid catalysts are required to direct the attack of nucleophiles towards the more substituted carbon of an epoxide (see: A. Mordini, S. Bindi, S. Pecchi, A. Capperucci, A. Degl'Innocenti, G. Reginato, *J. Org. Chem.* **1996**, *61*, 4466–4468). However, based on Baldwin's rules, we felt that the greater favorability of 5-*exo*-tet cyclization compared to the competing 6-*endo*-tet reaction would afford the desired product **21** in this case.
[12] K. C. Nicolaou, S. A. Snyder, A. Bigot, J. A. Pfefferkorn, *Angew. Chem.* **2000**, *112*, 1135–1138; *Angew. Chem. Int. Ed.* **2000**, *39*, 1093–1096.
[13] Crystallographic data (excluding structure factors) for structure **23** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147867. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[14] Although the conversion of secondary nitriles into ketones is known (see: R. W. Freerksen, S. J. Selikson, R. W. Wroble, K. S. Kyler, D. S. Watt, *J. Org. Chem.* **1983**, *48*, 4087–4096), this represents the first reported application of this methodology for the generation of lactones.
[15] T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508–7510.
[16] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.
[17] For an example of a ring-closing metathesis (RCM) in the presence of an N atom, see: A. Fürstner, J. Grabowski, C. W. Lehmann, *J. Org. Chem.* **1999**, *64*, 8275–8280. In our case, however, the chelating ability of the nitrogens in the indole and oxazole rings is likely to be poor and is not an overriding concern for RCM. For an example of RCM involving an oxazole, see: K. C. Nicolaou, H. Vallberg, N. P. King, F. Roschangar, Y. He, D. Vourloumis, C. G. Nicolaou, *Chem. Eur. J.* **1997**, *3*, 1957–1970.
[18] For pertinent discussion on the role of sterics in metathesis reactions, see: a) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413–4450; b) R. H. Grubbs, S. J. Miller, G. C. Fu, *Acc. Chem. Res.* **1995**, *28*, 446–452.
[19] For representative examples of the power of Wittig and Horner–Wadsworth–Emmons reactions to induce intramolecular macrocyclizations of complex substrates, see: a) I. Ernest, J. Gosteli, C. W. Greengrass, W. Holick, D. E. Jackman, H. R. Pfaendler, R. B. Woodward, *J. Am. Chem. Soc.* **1978**, *100*, 8214–8222; b) K. C. Nicolaou, S. P. Seitz, M. R. Pavia, N. A. Petasis, *J. Org. Chem.* **1979**, *44*, 4011–4013; c) K. C. Nicolaou, R. A. Daines, T. K. Chakraborty, Y. Ogawa, *J. Am. Chem. Soc.* **1988**, *110*, 4685–4696. For a recent review on the Wittig and HWE reactions in total synthesis, see: K. C. Nicolaou, M. W. Härter, J. L. Gunzner, A. Nadin, *Liebigs Ann.* **1997**, 1283–1301.
[20] To the best of our knowledge, this represents the first example of a phosphonate being successfully employed in a Suzuki-type coupling reaction.
[21] M. A. Blanchette, W. Choy, J. T. Davis, A. P. Essenfeld, S. Masamune, W. R. Roush, T. Sakai, *Tetrahedron Lett.* **1984**, *25*, 2183–2186.
[22] K. C. Nicolaou, A. E. Koumbis, S. A. Snyder, K. B. Simonsen, *Angew. Chem.* **2000**, *112*, 2629–2633; *Angew. Chem. Int. Ed.* **2000**, *39*, 2529–2533.

Triplet Di(9-anthryl)carbene Undergoes Trimerization[**]

Yasutake Takahashi, Masaaki Tomura,
Ken-ichi Yoshida, Shigeru Murata, and
Hideo Tomioka[*]

A large number of triplet carbenes have been characterized by electron paramagnetic resonance (EPR) spectroscopy.[1, 2] The principal information extracted from EPR spectra of triplet carbenes in randomly oriented matrices are the zero-field splitting (ZFS) parameters D and *E*, where *D* is a measure of the number of the unpaired electrons and thus allows the amount of delocalization in a carbene with conjugated π systems to be determined, while *E* measures the difference in the magnetic dipole interaction and, when weighted by *D*, allows one to estimate the bond angle at the carbene center.

Among the many triplet carbenes known, triplet di(9-anthryl)carbene (**1**) is unique as it shows the smallest *D* ($0.113\,\text{cm}^{-1}$) and *E* ($0.0011\,\text{cm}^{-1}$) values ever reported. This means that the carbene has almost linear and perpendicular geometry with extensive delocalization of the unpaired electrons into the anthryl portions of the molecule.[3]



1

Although these spectroscopic results suggest that the carbene should exhibit a reactivity that is substantially different from that observed for other diarylcarbenes, its chemistry has not been studied extensively. Herein we report that the carbene undergoes an unusual trimerization reaction, one that has never been observed before for any other carbenes.[4]

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[*] Prof. Dr. H. Tomioka, Prof. Dr. Y. Takahashi, K.-i. Yoshida
Chemistry Department for Materials
Faculty of Engineering, Mie University
Tsu, Mie 514-8507 (Japan)
Fax: (+81) 59-231-9416
E-mail: tomioka@chem.mie-u.ac.jp

Dr. M. Tomura
Research Center for Molecular Materials
Institute for Molecular Science
Okazaki, Aichi 444-8585 (Japan)

Prof. Dr. S. Murata
Department of Basic Science
Graduate School of Arts and Sciences, The University of Tokyo
Meguro, Tokyo 153-8902 (Japan)

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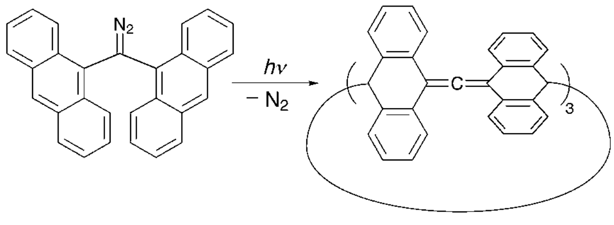
Irradiation ($\lambda > 300$ nm) of di(9-anthryl)diazomethane (**2**, 5×10^{-3} M) in degassed benzene caused rapid fading of the original orange diazo color with evolution of copious amounts of nitrogen gas to give a pale yellow solution [Eq. (1)]. After evaporation of the solvent, the resulting mixture was subjected to repeated gel-permeation chromatography, which eventually resulted in the isolation of white crystals (m.p. 332–333 °C) in 50% yield. The mass spectrum (FAB-MS) of the product showed a signal at 1099.1 (19.1%), which corresponds to the $M+1$ ion calculated for three di(anthryl)carbene units. Additional peaks were observed at 732.1 (19.6%) and 366 (100%), which correspond to the fragment formed as a result of the successive loss of the carbene unit from the trimer. Thus, the data clearly suggest that the main product is the trimer of di(anthryl)carbene, rather than a dimer as had been suspected earlier.[3b]



(1)

2 **3**

The structure of the trimer which best explains the NMR data is the one (**3**) formed as a result of a threefold coupling at positions 10 of the di(anthryl)carbenes. Thus, the ^{1}H NMR spectrum (500 MHz) showed the presence of eight aromatic proton signals ranging from $\delta = 7.79$ to 5.91 plus one signal at $\delta = 4.82$, which corresponds to a proton at a benzylic carbon atom.[5] The ^{13}C NMR spectrum (126 MHz), on the other hand, displayed a total of twelve aromatic sp^2 signals between $\delta = 136.42$ and 125.46. In addition, two signals were observed at $\delta = 208.34$ and 111.10, which can most probably be assigned as the central and terminal carbon atoms of the allenic subunit, respectively, and one sp^3 carbon atom at $\delta = 55.06$. The assignments are fully supported by two-dimensional NMR measurements (see the Supporting Information).

The molecular structure of the trimer was unambigously characterized by an X-ray crystallographic study. The analysis of **3** revealed that the compound has a complicated structure and contains a 27-membered ring with six fused benzo groups, which are oriented equatorially, and six bridging benzene subunits, three of which protrude axially on either side of the basic ring (Figure 1).[6, 7] The crystal lattice contains one crystallographically independent molecule of **3** and a solvent molecule (CH_2Cl_2) with 0.477 occupancy. No crystallographic symmetry element lies on **3**. The bond lengths in the allene moieties are normal,[8] but the allene moieties bend slightly (177.2°).[9] The 9-hydroanthracene moieties around the allene bonds are almost perpendicular to each other. The average value of the angles between the least-squares planes of the central six-membered rings at both ends of the allene bonds is 87.3°.

In spite of its sterically highly congested structure, trimer **3** exhibited surprising stability. It remained unchanged either upon heating in degassed benzene at 140 °C for 2 h or by irradiating it in degassed benzene with light ($\lambda > 300$ nm) for 2 h. However, it decomposed in air both thermally and photochemically to give anthraquinone as the main product.

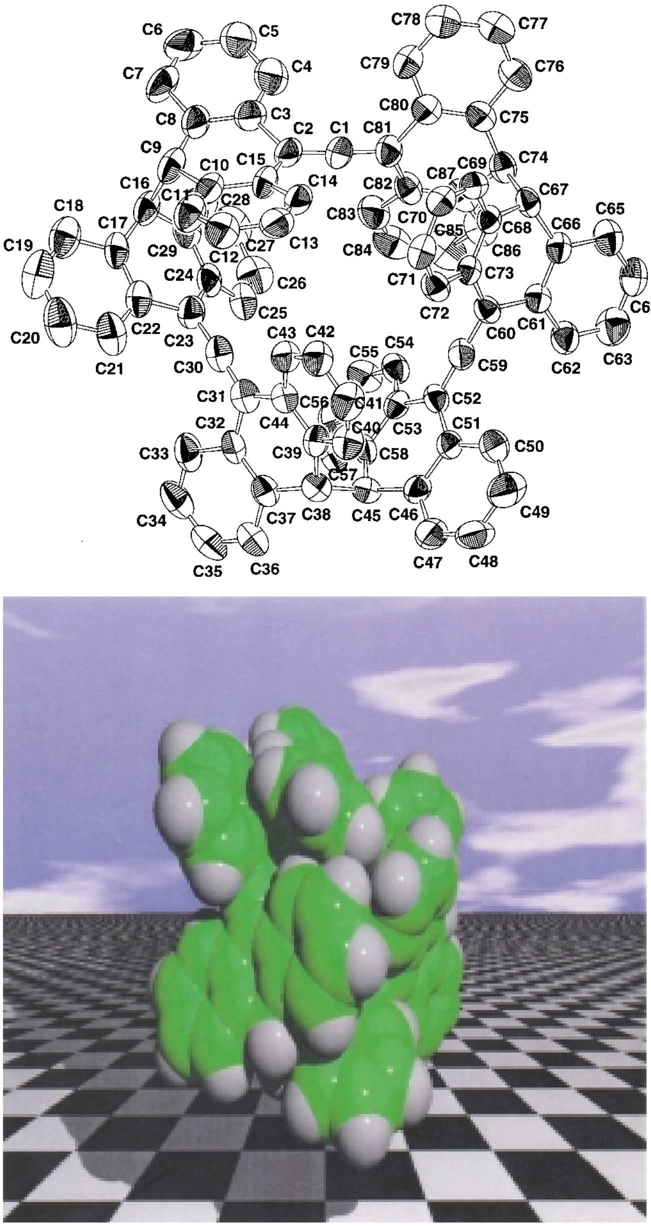


Figure 1. The X-ray crystallographic structure of the trimer **3**. Top: ORTEP drawing of **3** showing the labeling scheme; the solvent molecule (CH_2Cl_2) and the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-C2 1.320(12), C1-C81 1.322(12), C23-C30 1.331(12), C30-C31 1.307 12), C52-C59 1.320(10), C59-C60 1.322(11); C2-C1-C81 175.9(10), C23-C30-C31 176.4(10), C52-C59-C60 179.4(9). Bottom: Space-filling presentation of the structure.

Triplet carbenes, like radicals, can dimerize in a very fast and exothermic reaction. The efficiency of this process clearly depends on the concentration of the carbene. However, carbene dimers are usually not produced as major products in the reactions where "normal" carbenes are generated at room temperature by the steady-state photolysis of diazo precursors in solution. The probable reason for this is that nacsent and hence singlet carbenes react very efficiently with external reagents before they undergo intersystem crossing to form the triplet. Dimers may be formed instead by the attack of the singlet carbene on the precursor, whose concentration is much higher, and usually occurs in concomitance with the formation of a large amount of azine.[4] The formation of dimers as main products is observed only in the reaction of relatively stable triplet carbenes.[10] For example, di(2,4,6-trimethylphenyl)carbene (dimesitylcarbene) and hexachlorodiphenylcarbene produce the corresponding tetraarylethenes in high yield without any sign of the formation of azine even in a steady-state photolysis in solution at room temperature.[11, 12]

The trimerization of a carbene is completely unprecedented. The structure of trimer **3** clearly indicates that simple coupling at the carbenic carbon atom is not favored, as can be easily expected from the steric hindrance around the carbene center of **1**. Thus, ^{3}**1** is forced to undergo self-reaction at positions 10 where some spin density is localized.

A similar coupling reaction at an aromatic carbon atom is also suggested as a decaying pathway for sterically congested diarylcarbenes, as deduced from the rather dramatic effects of *para* substituents on the lifetime of the triplet carbenes.[13] For example, the lifetime of triplet diphenylcarbenes protected by four *ortho*-bromine groups is shown to increase by some two orders of magnitude when *para*-methyl substituents are replaced by *tert*-butyl groups. However, no products resulting from such a coupling have been isolated in this case.

The unusual formation of the product as a trimer in a significant amount as a result of such coupling at the aromatic moiety is rather unusual and clearly ascribable to its unique electronic and steric features. First, extensive delocalization of the unpaired electrons into the anthryl rings in ^{3}**1** is more prominent than that into phenyl rings in diphenylcarbenes. Second, 10,10′-diradical forms are clearly stabilized by the conjugation of each electron with the two fused aromatic rings and therefore have a sufficiently long lifetime to encounter each other in solution, even at room temperature. Inspection of the molecular structure of the trimer **3** suggests that the trimerization may take place in a way so as to avoid the congestion as much as possible. Thus, two "anthryl" groups in a diradical unit are connected by the allenic bond and hence situated perpendicular each other. Each coupling of the diradical unit at the 10 and 10′ positions takes place in a staggered fashion. In this way, three diradical units are suitably folded to eventually form the intricate cyclic compound. Intramolecular coupling of both ends at the dimer stage is clearly not favored, most probably because of a rather high activation barrier to ring closure that results from the very large distance between the radical centers. In a tetramer, on the other hand, steric repulsion arises between the "blades" as a consequence of a pertubation of the delicate balance between the linkers and blades.

These considerations explain, at least in part, the reason for this unusual trimerization process of ^{3}**1**. It is clear that further research, including the kinetics of the process, is neccessary. For this reason, studies are now in progress in our laboratory to fully understand this interesting behavior of ^{3}**1**.

Experimental Section

Crystal data for **3**: Trimer **3** was dissolved in CH_2Cl_2 and the solvent was evaporated slowly at ambient temperature for 5 d to give a single crystal of **3** that was suitable for X-ray crystallographic analysis. Crystal data for $C_{87}H_{54}(CH_2Cl_2)_{0.477}$: colorless plate, crystal dimensions $0.40 \times 0.10 \times 0.05$ mm^3, triclinic, space group $P1$, $a = 12.378(1)$, $b = 13.271(2)$, $c = 19.308(1)$ Å, $\alpha = 90.20(1)$, $\beta = 104.73(1)$, $\gamma = 100.30(1)^\circ$, $V = 3014.0(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.305$ Mg m^{-3}, $Cu_{k\alpha}$ radiation ($\lambda = 1.54178$ Å), $2\Theta_{max} = 148^\circ$. The data were collected on an Enraf-Nonius CAD4 diffractometer at 296 K. An absorption correction and a decay correction were not applied. The structure was solved by direct methods with SHELXS-86[6] and refined by full-matrix least-squares analysis on F^2 with SHELXL-93.[7] A total of 8513 reflections were collected, 8220 independent reflections were included in the refinement, 812 parameters, $R_1 = 0.0726$ and $wR_2 = 0.1695$ for data with $I > 2\sigma(I)$, GOF = 0.967, max. residual electron density 0.55 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined by using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-124125. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] A large number of triplet carbenes have been characterized by EPR spectroscopy since the pioneering work by Wasserman et al.: H. Wasserman, L. C. Snyder, W. A. Yager, *J. Chem. Phys.* **1964**, *41*, 1763; E. Wasserman, R. S. Hutton, *Acc. Chem. Res.* **1977**, *10*, 27.

[2] For reviews see: a) W. Sander, G. Bucher, S. Wierlacher, *Chem. Rev.* **1993**, *93*, 1583; b) H. Tomioka in *Advances in Strained and Interesting Molecules*, *Vol. 8* (Ed.: B. Halton), JAI, Stamford, **2000**, p. 83; c) A. M. Trozzolo, E. Wasserman in *Carbenes*, *Vol. 2* (Eds.: M. Jones, Jr., R. A. Moss), Wiley, New York, **1975**, p. 185.

[3] a) E. Wasserman, V. J. Kuck, W. A. Yager, R. S. Hutton, F. D. Greene, V. P. Abegg, N. M. Weinshenker, *J. Am. Chem. Soc.* **1971**, *93*, 6355; b) D. J. Astles, M. Girard, D. Griller, R.-J. Kolt, D. D. M. Wayner, *J. Org. Chem.* **1988**, *53*, 6053.

[4] a) W. Kirmse, *Carbene Chemistry*, Academic Press, New York, **1971**; b) R. A. Moss, M. Jones, Jr., *Carbenes*, *Vol. 1 and 2*, Wiley, New York, **1973** and **1975**; c) M. Regitz, *Carbene (oide)*, *Carbine*, Houben–Weyl, Thieme, Stuttgart, **1989**.

[5] The chemical shift is compatible with the benzylic position of 9,10,9′,10′-tetrahydro-[9,9′]-bianthryl: W. Huber, K. Müllen, *J. Chem. Soc. Chem. Commun.* **1980**, 698; C. M. Berk, A. Streitwieser, *J. Orgnomet. Chem.* **1980**, *197*, 123.

[6] G. M. Sheldrick, *Acta Crystalloger. Sect. A* **1990**, *46*, 467.

[7] G. M. Sheldrick, SHELXL-93, Program for refinement of crystal structures, University of Göttingen, Germany, **1993**.

[8] a) S. R. Landor, *The Chemistry of the Allenes*, *Vols. 1–3*, Academic Press, London, **1982**; b) H. Irngartinger, E. Kurda, H. Rodewald, A. Berndt, R. Bolze, K. Schlüter, *Chem. Ber.* **1982**, *115*, 967; c) M. Iyoda, Y. Kuwatani, M. Oda, Y. Kai, N. Kaneshita, N. Kasai, *Angew. Chem.* **1990**, *102*, 1077; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1062.

[9] Bis(biphenyl-2,2′-diyl)allene has been shown to have a bent allene bond (170.1°): E. Weber, W. Seichter, B. Hess, G. Will, H.-J. Dasting, *J. Phys. Org. Chem.* **1995**, *8*, 94.

[10] a) H. Tomioka, *Acc. Chem. Res.* **1997**, *30*, 315; b) H. Tomioka in *Advances in Carbene Chemistry*, *Vol. 2* (Ed.: U. Brinker), JAI, Samford, **1998**, p. 175.

[11] a) H. E. Zimmerman, D. H. Paskovich, *J. Am. Chem. Soc.* **1964**, *86*, 2149; b) H. Tomioka, K. Hirai, T. Nakayama, *J. Am. Chem. Soc.* **1993**, *115*, 1285; c) H. Tomioka, H. Okada, T. Watanabe, K. Banno, K. Komatsu, K. Hirai, *J. Am. Chem. Soc.* **1997**, *119*, 1582.

[12] A referee suggested that the trimer **3** could also be formed by the reaction of carbene **1** with the precursor diazomethane **2** as a result of **1** attacking **2** at position 10 and that this could be checked by examining the effect of the concentration of **2** on the rate of light-induced decay of **2**. We irradiated two samples containing different concentrations of **2** under identical conditions and found essentially no dependence of the rate on the concentration of **2**. We wish to thank the referee for the suggestion.

[13] H. Tomioka, M. Hattori, K. Hirai, S. Murata, *J. Am. Chem. Soc.* **1996**, *118*, 8723.