

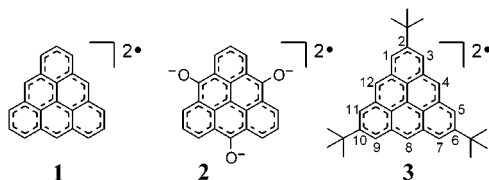
The First Detection of a Clar's Hydrocarbon, 2,6,10-Tri-*tert*-Butyltriangulene: A Ground-State Triplet of Non-Kekulé Polynuclear Benzenoid Hydrocarbon

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The C_3 -symmetric polycyclic hydrocarbon **1** known as triangulene or a Clar's hydrocarbon (IUPAC name: 4*H*,8*H*-dibenzo-[*cd,mn*]pyrene-4,8-diyl) dates back to a pioneering study by Clar in 1941.¹ Triangulene **1** is the most fundamental non-Kekulé polynuclear benzenoid (PNB) compound^{2–5} and is peculiar in that no Kekulé type formulas can be given, i.e., at least two carbon atoms are left without participating in the double bond network, giving rise to an open-shell electronic structure. Hückel molecular orbital calculations⁶ show that **1** has a pair of degenerate nonbonding molecular orbitals (NBMOs) with nondisjoint⁷ (or co-extensive⁸) nature as shown in Figure 1a. Thus, a triplet ground state is expected for **1** due to the occurrence of robust dynamic



π -spin polarization. Bearpark et al. estimated that the triplet state is located ca. 20 kcal mol⁻¹ (1×10^4 K; 7×10^3 cm⁻¹) lower than the singlet state.⁹ The theory also shows that large spin densities in the triplet ground state appear at the edge sites of the

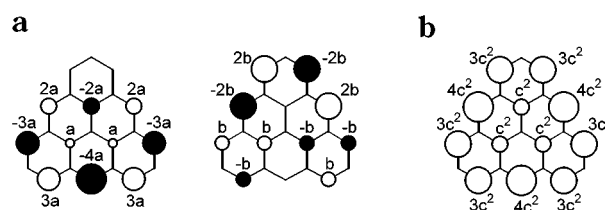


Figure 1. (a) A pair of degenerate π -NBMOs of triangulene **1** calculated by Hückel MO theory, showing the nondisjoint nature.⁷ The coefficients are $a = 1/\sqrt{66}$ and $b = 1/\sqrt{22}$. (b) Spin density distribution of the triplet state of **1**. The coefficient is $c^2 = 2/33$.

molecule as shown in Figure 1b, giving rise to a highly reactive neutral state. Synthesis and chemical identification of **1** have not only been long-standing issues in chemistry since Clar's proposal,¹ but have recently also attracted much attention in terms of materials challenge in the field of molecule-based magnetics.¹⁰ Extended triangulenes with large spin multiplicities retain the salient feature of the spin density distribution of the nondisjoint degenerate NBMOs.

The first attempt to generate **1** from the corresponding precursor was made by Clar et al., but only the polymerized product was obtained,² demonstrating the kinetic instability of the molecule. Later, Murata et al. generated a closed-shell dianion **1**²⁻ and related PNBs.¹¹ In recent years, Bushby's group attempted to make a series of non-Kekulé PNBs with heteroatomic modification by chemical reduction of the corresponding diketones.^{4,5} Only the ground-state triplet of trioxytriangulene **2** was detected by ESR spectroscopy,⁴ while the other derivatives appeared to be ESR-silent.⁵ The introduction of heteroatoms lifts the degeneracy of the NBMOs, causing kinetic exchange interaction to dominate over dynamic spin polarization in the parent π -systems. In this work, we have introduced three *tert*-butyl groups on the carbon sites with nodes in the NBMOs of **1** for protecting the reactive carbon sites as well as minimizing the electronic perturbation.^{12,13} Here, we report on the synthesis and ESR detection of a Clar's hydrocarbon, 2,6,10-tri-*tert*-butyltriangulene **3**, in a triplet ground state as the first example of a genuine non-Kekulé PNB high-spin hydrocarbon, characterizing intermediate species derived from the precursor in terms of ¹H ENDOR/TRIPLE spectroscopy.

The precursor, dihydrotriangulene **12** (Scheme 1), and 10 equiv of *p*-chloranil were dissolved in toluene in an ESR quartz tube (5×10^{-3} M). The sample was degassed and sealed after several freeze–pump–thaw cycles, and kept at 195 K before ESR measurements. Figure 2a suggests that at the initial reaction stage an electron-transfer took place from **12** to *p*-chloranil, generating **12**^{•+}, which most accounts for the observed spectrum.¹⁴ On raising the temperature, the color of the solution gradually changed from pale yellow to orange, and complicated isotropic hyperfine ESR spectra appeared and showed time-dependent variations (Figure 2a,b), indicating that the reaction proceeded. At this intermediate

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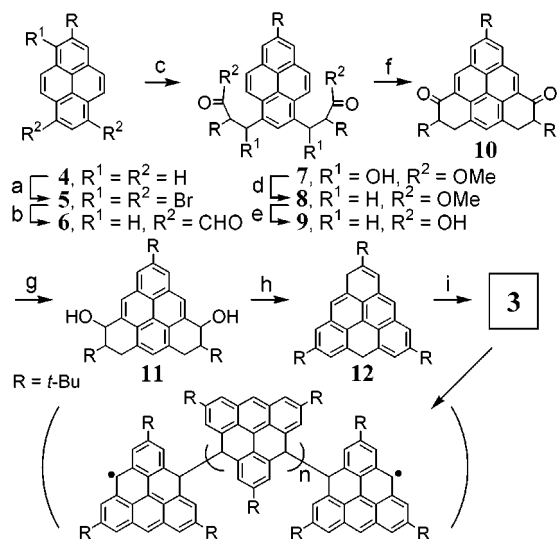
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Scheme 1^a

^a Reagents and conditions: (a) Br₂, CH₂Cl₂, room temperature, 67%; (b) 15 equiv of *t*-BuLi, -78 °C, then 23 equiv of DMF, THF, -78 °C, 79%; (c) *t*-BuCHBrCOOMe, Zn, I₂, benzene, reflux; (f) (COCl)₂, reflux then AlCl₃, CH₂Cl₂, -78 °C, 45% from **8**; (g) LiAlH₄, THF, room temperature, 74%; (h) PTSA, benzene, reflux, 97%; (i) *p*-chloranil, toluene.

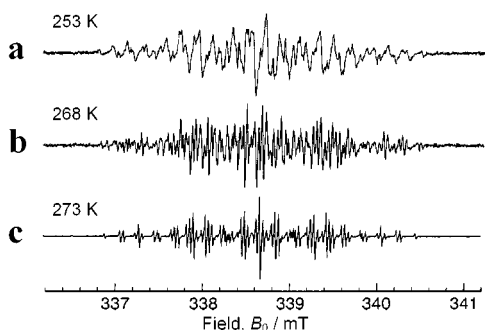


Figure 2. Liquid-phase ESR spectra generated in a toluene solution of **12** and *p*-chloranil. The microwave frequency used is 9.49327 GHz. (a) The initial reaction stage: no appreciable change for several hours at 253 K. (b) The intermediate stage: the spectrum is the superposition of the spectra a and c. (c) The final stage: the spectrum observed after gradual warming over ca. 10 h.

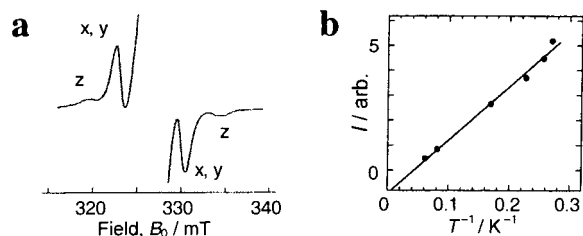


Figure 3. (a) Observed triplet-state ESR spectrum of **3** with monoradical species in a frozen toluene matrix at 123 K; *x*, *y*, and *z* denote the canonical absorption peaks. The microwave frequency used is 9.6190 GHz. (b) Plot of the temperature dependence of the triplet signal intensity *I* versus $1/T$ from 3.7–16 K.

stage, rapid freezing of the sample gave a superposition of spectra from spin-doublet states and a typical fine-structure ESR spectrum of a triplet state with an axial symmetry (Figure 3a). The spin Hamiltonian parameters were determined by the spectral simulation to be $S = 1$, $g = 2.003$, $|D|/hc = 0.0073 \text{ cm}^{-1}$, and $|E|/hc \sim 0 \text{ cm}^{-1}$, which are attributed to triangulene **3**, a genuine hydrocarbon structure with a 3-fold rotation axis. As expected

from the small D value and vanishing E value, the forbidden transition ($\Delta M_S = \pm 2$) was extremely weak.¹⁵ The linear dependence of the triplet signal intensity I on $1/T$ (Figure 3b) shows that the observed triplet is the electronic ground state with other states located far above. The result is in good agreement with the theoretical prediction for **1**.⁹

The observed D value provides information on the ground-state spin structure of triangulene **3**. According to the point-dipole approximation model, two dipolar spins in **3** are assumed to circulate synchronously at a maximum inter-spin distance r_0 . In this model, the maximum distance ensures Pauli's exclusion principle and the mean inter-spin distance r_0 is derived from the expression $D = (3\mu_0/16\pi)(g\beta)^2/r_0^3 (>0)$, where μ_0 is the permeability in a vacuum, g stands for the g -value of the triplet state, and β is the Bohr magneton. The principal Z axis of the D tensor in this model points parallel to the 3-fold rotation axis of **3**. The calculation gives $r_0 = 5.64 \text{ \AA}$ for **3**, being consistent with the size of the molecular plane and the salient feature of the spin density distribution in the NBMOs. Compared with the D value for **2** (0.0064 cm^{-1})⁴ and $r_0 = 5.88 \text{ \AA}$, a large amount of spin delocalization onto the three O-sites in **2** provides a rationale for the larger r_0 for **2**. A point-dipole calculation based on an MO method utilizing Slater-MO-determinants for the NBMOs was also carried out to give $D/hc = +0.0168 \text{ cm}^{-1}$ and $E/hc = 0 \text{ cm}^{-1}$.¹⁶

Further reaction at 273 K gave a marked decay of the triplet signal intensity, showing that **3** is not kinetically stable in solution. At the final reaction stage a simple hyperfine structure due to doublet species with $g = 2.0028$ appeared in the ESR spectra (Figure 2c). The ¹H ENDOR/TRIPLE study for the final product revealed that the ESR spectra were well described by four kinds of ¹H-hyperfine couplings, each of which corresponds to a pair of nearly equivalent protons (-0.755 , -0.621 , -0.213 , and -0.174 mT), as shown in Figure 2c. The ¹H couplings were reasonably explained by assuming doublet radicals having triangulene-based molecular structures, in which one site of 4-, 8-, or 12-positions of **3** was replaced by an sp^3 carbon derived from an intermolecular chemical bond between the monomers, leading to oligomers ($n \geq 0$; $n = 0$ for a dimer) such as **13** given in Scheme 1. When the reaction proceeds at 273 K, the solution becomes viscous, suggesting the occurrence of higher degrees of the oligomerization. The singly occupied MO of the resulting 21π system becomes similar to Ψ_{12} in Figure 1a, which accounts well for the observed hyperfine couplings. At ambient temperature the partial exposure of these reactive carbon sites with the largest spin density (Figure 1b) allows **3** to form the final products **13**, although **3** is stable enough to give the triplet ESR spectrum in a rigid glass. The present study illustrates the effective steric protection by bulky groups to stabilize the reactive parent hydrocarbon **1**, but the partial protection does not prevent **3** from undergoing the intermolecular coupling. Further stabilization of triangulene by additional substitutions is under way to isolate genuine non-Kekulé PNBs in the crystalline state.

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Supporting Information Available: Experimental procedures, spin density distributions of 2D PNBs, and ESR/ENDOR/TRIPLE spectra for new compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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