Supporting Information
The First Crystal Structure of a Monomeric Phenoxyl Radical: 2,4,6-Tri-*tert*-butylphenoxyl Radical

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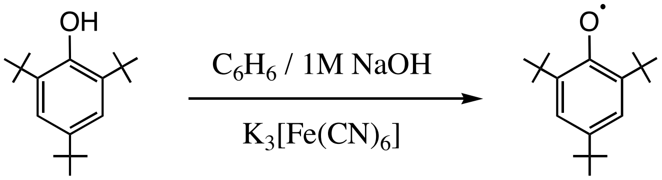
I. General Experimental

Unless otherwise noted, all reagents were purchased from Aldrich and solvents from Fischer. Sodium hydroxide pellets were purchased from J. T. Baker. Acetonitrile was purchased from Burdick and Jackson (low-water brand) and stored in an argon-pressurized stainless steel drum plumbed directly into a glovebox. Deionized water was used in synthesis of 2,4,6-tri-*t*-butyl phenoxyl radical (**^{t}Bu$_3$ArO$^{\bullet}$**). Synthesis and characterization of **^{t}Bu$_3$ArO$^{\bullet}$** were performed under nitrogen, but all work with 2,4,6-tri-*t*-butyl phenol (**^{t}Bu$_3$ArOH**) was performed under air, after it was recrystallized in 95% ethanol. UV-Vis spectra were obtained using a Hewlett-Packard 8453 diode array spectrophotometer. Elemental analysis was performed by Atlantic Microlab, Inc.

II. Synthesis of ^{t}Bu$_3$ArO$^{\bullet}$



The synthesis of 2,4,6-tri-*t*-butyl phenoxyl radical (**^{t}Bu$_3$ArO$^{\bullet}$**) involved a modification of a literature procedure, and performed in a swivel-frit apparatus.[1] The parent phenol, 2,4,6-tri-*t*-butyl phenol (**^{t}Bu$_3$ArOH**, 1.25 g, 4.76 mmol), was dissolved in 80 mL benzene, and 15 mL of 1M NaOH was added. The solution was degassed using two freeze-pump-thaw cycles. The solution was frozen again, potassium ferricyanide (3.94 g, 11.97 mmol) was added, followed by another freeze-pump-thaw cycle. Upon warming to room temperature, the reaction was allowed to stir for two hours under nitrogen. The solvent was removed *in vacuo*, 100 mL diethyl ether was vac-transferred to the flask, and the solution was filtered. The diethyl ether was removed *in vacuo* from the filtrate, and the dark blue powder was redissolved in approximately 100 mL acetonitrile. Dark blue crystals of **^{t}Bu$_3$ArO$^{\bullet}$** grew overnight (0.70 g, 56%) in the dark at -30 °C. X-ray quality crystals were grown from the mother liquor over the course of 1 week. Elemental analysis calculated for $C_{18}H_{29}O$: C, 82.70; H, 11.18; N, 0.00. Found: C, 82.65; H, 11.27; N, 0.00.

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(1) A. R. Forrester, J. M. Hay, and R. H. Thomson, *Organic Chemistry of Stable Free Radicals*, Academic Press Inc. Ltd, London, 1968, pp 281-282; C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Am. Chem. Soc.*, 1955, **78**, 2002.

III. Calculation of Extinction Coefficient

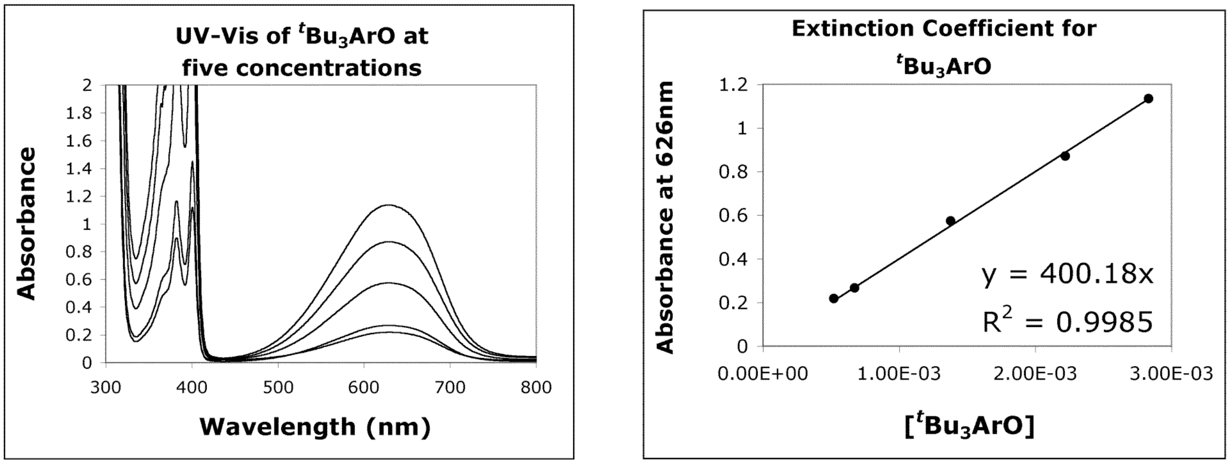

Figure S1. UV-Visible spectra of **^{t}Bu$_3$ArO$^\bullet$** at five concentrations (*left*). Plot of [**^{t}Bu$_3$ArO$^\bullet$**] versus absorbance at λ_{max} = 626 nm (*right*).

626 nm: $\varepsilon_{626}{}^{a} = 400 \pm 10\ M^{-1}cm^{-1}$
383 nm: $\varepsilon_{383}{}^{b} = 1720 \pm 100\ M^{-1}cm^{-1}$
400 nm: $\varepsilon_{400}{}^{b} = 2120 \pm 130\ M^{-1}cm^{-1}$

[a] Value obtained from slope of plot shown in Figure S1.
[b] Value is an average obtained from two lowest concentrations.

IV. Calculations

All calculations were performed using Gaussian Development Version, Revision D.02.[2] All geometries were confirmed to be local minima by IR frequency analysis. For the reported Mulliken spin densities a positive value indicates α spin, a negative value indicates β spin. Percentage spin density is relative to the total unpaired α spin density on all atoms in the molecule.

Table S1. Calculated bond lengths (Å)

	X-ray	UB3LYP/ 6-31G*	UBH&HLYP/ 6-31G*	UMPW1K/ 6-31G*	UHF/ 6-31G*	UMP2/ 6-31G*	ROBH&HLYP/ 6-31G*	ROHF/ 6-31G*
C1-O	1.246(2)	1.258	1.244	1.267	1.243	1.224	1.240	1.214
C1-C2	1.4713(14)	1.473	1.460	1.481	1.462	1.482	1.463	1.480
C2-C3	1.3673(18)	1.385	1.376	1.391	1.391	1.358	1.373	1.363
C3-C4	1.4068(15)	1.410	1.401	1.416	1.409	1.400	1.399	1.406
C3'-C4	1.4068(15)	1.417	1.409	1.422	1.416	1.413	1.423	1.423
C2'-C3'	1.3673(18)	1.378	1.369	1.386	1.385	1.346	1.365	1.352
C1-C2'	1.4713(14)	1.475	1.463	1.481	1.464	1.486	1.466	1.483
MSE[a]		0.0085	-0.0024	0.0152	0.0047	-0.0038	-0.0013	-0.0023
MUE[b]		0.0085	0.0057	0.0152	0.0104	0.013	0.0075	0.0126
Bond alt[c]	0.037	0.034	0.033	0.034	0.028	0.047	0.036	0.044

[a] Mean signed error [b] Mean unsigned error [c] Bond alternation = mean deviation from the average C-C bond length.

Table S2. Calculated bond lengths (Å) using larger basis sets

	X-ray	UMPW1K/ 6-31+G**	UB3LYP/ 6-311G*	UB3LYP/ 6-31+G**	UB3LYP/ EPR2
C1-O	1.246(2)	1.267	1.250	1.258	1.258
C1-C2	1.4713(14)	1.482	1.474	1.475	1.479
C2-C3	1.3673(18)	1.392	1.382	1.386	1.390
C3-C4	1.4068(15)	1.417	1.408	1.411	1.415
C3'-C4	1.4068(15)	1.423	1.415	1.418	1.423
C2'-C3'	1.3673(18)	1.386	1.375	1.380	1.384
C1-C2'	1.4713(14)	1.482	1.475	1.476	1.481
MSE[a]		0.0152	0.0060	0.0096	0.0133
MUE[b]		0.0152	0.0060	0.0096	0.0133
Bond alt[c]	0.037	0.034	0.035	0.034	0.034

[a] Mean signed error [b] Mean unsigned error [c] Bond alternation = mean deviation from the average C-C bond length.

Table S3. Calculated spin density and $\langle S^2 \rangle$ values

	UB3LYP/ 6-31G*	UBH&HLYP /6-31G*	UMPW1K/ 6-31G*	UHF/ 6-31G*	UMP2/ 6-31G*	UB3LYP/ 6-311G*	UB3LYP/ 6-31+G**	UB3LYP/ EPR2
$\langle S^2 \rangle$	0.780	0.848	0.761	1.325	0.944	0.778	0.779	0.779
O	0.366	0.426	0.320	0.632	0.544	0.348	0.349	0.345
C1	-0.052	-0.160	-0.028	-0.597	-0.516	-0.039	-0.067	-0.029
C2	0.316	0.428	0.308	0.882	0.834	0.314	0.345	0.304
C2'	0.272	0.381	0.266	0.857	0.786	0.268	0.300	0.258
C3	-0.163	-0.295	-0.167	-0.802	-0.750	-0.154	-0.204	-0.136
C3'	-0.152	-0.280	-0.156	-0.798	-0.733	-0.141	-0.194	-0.126
C4	0.395	0.505	0.439	0.909	0.912	0.391	0.462	0.365
o-*C*Me$_3$	-0.026	-0.039	-0.034	-0.097	-0.098	-0.026	-0.035	-0.019
o-*C'*Me$_3$	-0.021	-0.034	-0.032	-0.099	-0.094	-0.022	-0.037	-0.019
p-*C*Me$_3$	-0.018	-0.030	-0.030	-0.095	-0.087	-0.019	-0.033	-0.016

Table S4. Summary of calculated percent spin density/ bond alternation/ C-O length for all calculations of ^{t}Bu$_3$PhO$^\bullet$

	rCO	bond alternation[a]	O spin	C4 spin
Crystal Structure	1.246(2)	0.0374		
UB3LYP/6-31G*	1.258	0.0340	25.4%	27.4%
UBH&HLYP/6-31G*	1.244	0.0325	23.0%	27.3%
UMPW1K/6-31G*	1.267	0.0344	22.0%	30.2%
UHF/6-31G*	1.243	0.0278	18.0%	25.8%
UMP2/6-31G*	1.224	0.0466	16.4%	27.6%
UB3LYP/6-311G*	1.250	0.0353	24.7%	27.7%
UB3LYP/6-31+G**	1.258	0.0341	22.1%	29.3%
UB3LYP/EPR-II	1.258	0.0344	25.5%	27.0%

[a] The mean deviation from the average C-C bond length.

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(2) All calculations performed using Gaussian Development Version, Revision D.02: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

V. X-ray Crystal Structure of $^t\mathrm{Bu_3ArO}^\bullet$

General procedure. A dark blue needle was cut and mounted on a glass capillary with oil. Data were collected at -143°C.

Crystal-to-detector distance was 30 mm and exposure time was 50 seconds per degree for all sets. The scan width was 2.0°. Data collection was 99.3% complete to 25° in ϑ. A total of 21990 partial and complete reflections were collected covering the indices, h = -20 to 20, k = -12 to 12, l = -15 to 15. 2037 reflections were symmetry independent and the $R_{\text{int}} = 0.0780$ indicated that the data was close to average quality (0.07).

Indexing and unit cell refinement indicated a monoclinic lattice. The space group was found to be C 2/c (No. 15).

The data was integrated and scaled using hkl-SCALEPACK. This program applies a multiplicative correction factor (S) to the observed intensities (I) and has the following form:

$S = \exp(2B(\sin q/\lambda)^2)/\ \mathrm{scale}$

S is calculated from the scale and the B factor is determined for each frame and is then applied to I to give the corrected intensity (I_{corr}).

Solution by direct methods (SHELXS97) produced a complete heavy atom phasing model consistent with the proposed structure.

All hydrogen atoms were located using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

Table S5. Crystal data and structure refinement for **$^{t}\mathbf{Bu_3ArO}^{\bullet}$**

Empirical formula	C18 H29 O	
Formula weight	261.43	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal description/color	cut-block / blue	
Crystal system, space group	Monoclinic, c 2/c	
Unit cell dimensions	a = 15.6814(7)	$\alpha = 90°$
	b = 9.5268(5)	$\beta = 94.948(3)°$
	c = 11.3995(5)	$\gamma = 90°$
Volume	1696.58(14) Å^3	
Z, Calculated density	4, 1.023 Mg/m^3	
Absorption coefficient	0.061 mm^{-1}	
F(000)	580	
Crystal size	0.10 x 0.10 x 0.10 mm	
Reflections for indexing	84	
Theta range for data collection	2.50 to 28.47°	
Index ranges	$-20 \le h \le 20$, $-12 \le k \le 12$, $-15 \le l \le 15$	
Reflections collected / unique	3809 / 2037 [$R_{\mathrm{int}} = 0.0780$]	
Completeness to theta	25.00 99.3%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9940 and 0.9940	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2037 / 0 / 105	
Goodness-of-fit on F^2	$S = 0.985$	
Final R indices [$I > 2\sigma(I)$]	*$R1 = 0.0569$, $wR2 = 0.1471$	
R indices (all data)	$R1 = 0.0899$, *$wR2 = 0.1675$	
Largest diff. peak and hole	0.389 and -0.200	

VI. X-ray Crystal Structure of ^{t}Bu$_3$ArOH

General procedure. A clear crystal was cut and mounted on a glass capillary with oil. Data were collected at -143°C.

Crystal-to-detector distance was 30 mm and exposure time was 60 seconds per degree for all sets. The scan width was 2.0°. Data collection was 98.8% complete to 25° in ϑ. A total of 24564 partial and complete reflections were collected covering the indices, h = -12 to 12, k = -21 to 21, l = -24 to 24. 1347 reflections were symmetry independent and the R_{int} = 0.0623 indicated that the data was close to average quality (0.07).

Indexing and unit cell refinement indicated a monoclinic lattice. The space group was found to be C 2/c (No. 15).

The data was integrated and scaled using hkl-SCALEPACK. This program applies a multiplicative correction factor (S) to the observed intensities (I) and has the following form:

$S = \exp(2B(\sin q/\lambda)^2)/\ \text{scale}$

S is calculated from the scale and the B factor is determined for each frame and is then applied to I to give the corrected intensity (I_{corr}).

Solution by direct methods (SHELXS97) produced a complete heavy atom phasing model consistent with the proposed structure.

All hydrogen atoms were located using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

Comments. The structure of **^{t}Bu$_3$ArOH** was solved using monoclinic C 2/c. The space group as solved does not include the three-fold axis resulting from disorder, and the structure cannot be solved in a space group of higher symmetry due to software constraints. The hydroxy group is equally disordered at the C1, C3, and C5 positions, and all *tert*-butyl groups are also equally disordered.

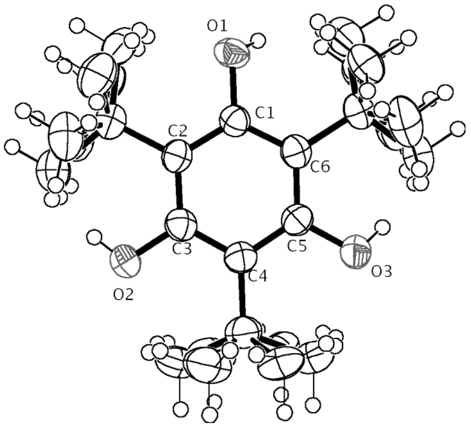

Figure S2. X-ray crystal structure of **^{t}Bu$_3$ArOH**.

Table S6. Crystal data and structure refinement for **^{t}Bu$_3$ArOH**

Empirical formula	C18 O H30[a]	
Formula weight	262.44	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal description/color	cut-block / clear	
Crystal system, space group	Monoclinic, C 2/c	
Unit cell dimensions	a = 10.0648(5)	α = 90°
	b = 17.4311(9)	β = 90.185(3)°
	c = 19.6355(9)	γ = 90°
Volume	3444.8(3) Å^3	
Z, Calculated density	8, 1.003 Mg/m^3	
Absorption coefficient	0.060 mm^{-1}	
F(000)	1151	
Crystal size	0.10 x 0.10 x 0.10 mm	
Reflections for indexing	82	
Theta range for data collection	2.07 to 26.96°	
Index ranges	$-12 \leq h \leq 12$, $-21 \leq k \leq 21$, $-24 \leq l \leq 24$	
Reflections collected / unique	6571 / 3479 [R_{int} = 0.0623]	
Completeness to theta	25.00 98.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9947 and 0.9947	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3479 / 0 / 292	
Goodness-of-fit on F^2	S = 0.944	
Final R indices [I > 2σ(I)]	*R1 = 0.0643, wR2 = 0.1479	
R indices (all data)	R1 = 0.1640, *wR2 = 0.1983	
Largest diff. peak and hole	0.145 and -0.158	

[a] The structure was solved with one-third of a hydroxyl group at three positions without two-thirds of a hydrogen atom, so the crystallographic formula is C18 O0.99 H 27.99.

Table S7. Important bond lengths (Å) for **^{t}Bu$_3$ArOH**

Bond	Length (Å)
O1–C1	1.386(4)
O2–C3	1.362(4)
O3–C5	1.371(4)
C1–C6	1.407(3)
C1–C2	1.391(3)
C2–C3	1.410(3)
C3–C4	1.398(3)
C4–C5	1.399(3)
C5–C6	1.400(3)