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A C–C Bonded Phenoxy Radical Dimer with a Zero Bond Dissociation Free Energy

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Abstract

The 2,6-di-*tert*-butyl-4-methoxy-phenoxy radical is shown to dimerize in solution and in the solid state. The X-ray crystal structure for the dimer, the first for a *para*-coupled phenoxy radical, reveals a bond length of 1.6055(23) Å for the 4-4' C–C bond. This is significantly longer than typical C–C bonds. Solution equilibrium studies using both optical and IR spectroscopies show that the K_{eq} for dissociation is 1.3 ± 0.2 M at 20 °C, indicating a C–C bond dissociation free energy of -0.15 ± 0.1 kcal mol⁻¹. Van't Hoff analysis gives an exceptionally small bond dissociation enthalpy (BDE) of 6.1 ± 0.5 kcal mol⁻¹. To our knowledge, this is the weakest BDE measured for a C–C bond. This very weak bond shows a large deviation from the correlation of C–C bond lengths and strengths, but the computed force constant follows Badger's rule.

Weak chemical bonds have long attracted interest as they test aspects of chemists' intuition regarding the nature of bonding and relationships among bond strength, bond length and other parameters.^{1–4} Zavitsas described a linear correlation of C–C bond lengths and bond strengths over a >200 kcal mol⁻¹ range,¹ and the long-standing Badger's rule relates bond length and force constant.² We describe here the characterization of a phenoxy radical dimer with an extremely weak C–C bond.

Phenoxy radicals are important in biology, in natural and synthetic antioxidant chemistry, and are increasingly studied in radical and proton-coupled electron transfer (PCET) reactions.⁵ Phenoxy radicals that are protected at the 2, 4 and 6-positions, such as 2,6-di-*tert*-butyl-4-methoxy-phenoxy radical (*t*Bu₂(MeO)ArO•), are unusually stable in oxygen-free solutions.⁶ In 1955, Mueller and Ley found that the radical content of *t*Bu₂(MeO)ArO• is not quantitative by magnetic susceptibility, and proposed equilibrium formation of the 4-4'-bis-cyclohexadienone dimer (*t*Bu₂(MeO)ArO)₂ (Figure 1A).⁷ Reported here are the X-ray crystal structure and dissociation thermochemistry of the dimer.

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Supporting Information.

Experimental details, analyses, X-ray crystallographic data and computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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tBu₂(MeO)ArO[•] was prepared by treating 2,6-di-*tert*-butyl-4-methoxyphenol with potassium ferricyanide in a biphasic medium of benzene and 1 M aqueous sodium hydroxide, following a related procedure.⁸ The resulting purple oil was crystallized from dry, oxygen-free acetonitrile at -30 °C forming light yellow crystals. The X-ray crystal structure revealed the *para*-coupled dimer (Figure 1B). The dimer lies on a crystallographic inversion center in the monoclinic *C*2/*c* space group. To our knowledge, this is the first X-ray crystal structure reported for a *para*-coupled phenoxyl radical dimer.

The metrical data for the structure of (***t***Bu₂(MeO)ArO)₂ (Table 1) are consistent with the line structure in Figure 1A. The C1–O1 bond length of 1.2227(15) is characteristic of a C=O double bond. The 1.34 Å C2–C3 and C5–C6 bond distances are typical of C=C double bonds, while the C1–C2, C3–C4, C4–C5, and C6–C1 bond distances are slightly longer than 1.47 Å sp³–sp² single bonds. The carbon-carbon bond connecting the two halves of the dimer, C4–C4a, is 1.6055(23) Å, which is much longer than the standard 1.54 Å sp³–sp³ bond distance.⁹ The recently reported structure of the 9,10-dialkoxyanthracene radical cation dimer has a 1.637(5) Å C–C bond,¹⁰ and C–C bond lengths of other similar structures range from 1.59 – 1.64 Å.^{11,12}

The bis-cyclohexadienone structure was proposed by Mueller and Ley based on quinone-like stretches at ~1600 cm⁻¹ and ~1650 cm⁻¹ in the solution IR spectrum of ***t***Bu₂(MeO)ArO[•].⁷ An IR spectrum of our isolated solid dimer, obtained as a KBr pellet, shows two strong IR stretches at 1646 cm⁻¹ and 1667 cm⁻¹ (Figure 2A).

DFT calculations of the dimer (M06-2X/6-31+G(2d,2p)) gave gas-phase bond lengths in close agreement with measured solid-state distances (Table 1).¹³ The computed C4–C4a bond length is of 1.6065 Å is within 3σ of the measured distance. The M06-2X functional was chosen because it accounts for long-range noncovalent interactions that can be an important factor in long C–C bonds.^{1b} The calculated gas-phase vibrational frequencies are less close to the measured frequencies (Figures 2 and S4, S5 of the Supporting Information). For instance, the C=O/C=C stretching frequencies are calculated to be 1629, two doubly degenerate signals at 1660, and 1690 cm⁻¹, versus 1622, 1632, 1646 and 1667 cm⁻¹ both in the solid state (KBr pellet) and in solution (CCl₄) (Table S2).

The equilibrium constant for dimer dissociation (*K*_{eq}) at 20 ± 2 °C was determined by solution IR spectroscopy in CCl₄. At low concentrations only the monomer ***t***Bu₂(MeO)ArO[•] was observed, while at 50 mM the dimer was evident from its bands at 1646 cm⁻¹ and 1667 cm⁻¹ (Figure 2B). The concentrations of ***t***Bu₂(MeO)ArO[•] in solutions where both monomer and dimer were present was determined from the relatively weak extinction coefficient at 1292 cm⁻¹ (Figure S6).¹⁴ The dimer concentrations were then calculated using mass balance. Fitting the data to the equilibrium in Figure 1 (Figure S8) gave *K*_{eq} = 1.3 ± 0.2 M at 20 °C. This corresponds to a free energy of -0.15 ± 0.1 kcal mol⁻¹.

Equilibrium constants at temperatures from -20 to +20 °C were determined by measuring the optical absorbance of ***t***Bu₂(MeO)ArO[•] in CCl₄ solutions (Figure 3). For concentrated solutions, 1- or 2-mm pathlength cuvettes were used and the absorbance of ***t***Bu₂(MeO)ArO[•]

was measured at 605 nm rather than at the peak maximum. A plot of absorbance vs. [***t***Bu₂(MeO)ArO•] for dilute (<20 mM) solutions of ***t***Bu₂(MeO)ArO• at 22 ± 1 °C was linear with $\epsilon = 44 \text{ M}^{-1} \text{ cm}^{-1}$ at 605 nm (Figure S1). At concentrations above 20 mM and at lower temperatures, such Beer's Law plots were non-linear, suggesting loss of ***t***Bu₂(MeO)ArO• to form the dimer (Figure S2). The data are well fit by the equilibrium in Figure 1, with the assumption of mass balance (Figure S3). The K_{eq} at 20 °C was found to be $1.4 \pm 0.3 \text{ M}^{-1}$, in excellent agreement with the value from the IR study. A van't Hoff plot of the K_{eq} values from -20 to +20 °C (Figure 3; Table S1) gives the enthalpy and entropy of dimer dissociation: $H^\circ = 6.1 \pm 0.5 \text{ kcal mol}^{-1}$ and $S^\circ = 21 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$.

(***t***Bu₂OMeArO)₂ has an extremely weak C–C bond, with a bond dissociation enthalpy (BDE) of 6.1 kcal mol⁻¹. To our knowledge, this is the weakest C–C bond that has been experimentally measured. It is 8 kcal mol⁻¹ weaker than the BDE estimates of Mahoney and Weiner for less crowded phenoxyl radical dimers.¹⁵ Gomberg's triphenylmethyl radical forms a stronger C–C bond (BDE = 11 kcal mol⁻¹) and is only slightly dissociated in concentrated solutions.¹⁶ Phenalenyl radical dimers with BDEs of 9.5 – 14 kcal mol⁻¹ have been described.¹⁷ Scaiano *et al.* have reported BDEs of 15–26 kcal mol⁻¹ for dimers of stabilized carbon-centered radicals with similar C–C bond distances.¹² A formally iron(I)-pyridine complex was recently found to undergo reversible coupling to a 4,4'-dimer, with a BDE likely similar to that in Gomberg's dimer.¹⁸ More bulky derivatives such as (4-*t*BuPh)₃C•¹⁹ and 2,4,6-*t*Bu₃C₆H₂O• do not dimerize and therefore must form weaker C–C bonds than ***t***Bu₂(MeO)ArO•.

The C–C bond in (***t***Bu₂OMeArO)₂ is much weaker than would have been expected based on its bond distance of 1.6055(23) Å. A linear correlation between C–C bond length and BDE has been proposed (Figure 4A).¹ It would predict a BDE of >50 kcal mol⁻¹ for this bond length, or a bond length of >1.7 Å for such a weak C–C bond. Other deviations have been reported and discussed.²⁰ For example, the points for Scaiano's C–C dimers are included in Figure 4A.¹² Also included are recently reported alkanes with long C-C bonds (up to 1.71 Å) but high attractive dispersion forces, which deviate from the correlation in the opposite direction.²¹

The deviation of (***t***Bu₂OMeArO)₂ from this correlation is likely due to the large stabilization energy of the monomeric phenoxyl radical associated with structural rearrangements upon dissociation.^{12,17,22} This stabilization energy was computed using a single point calculation of the ***t***Bu₂(MeO)ArO• monomer at the optimized geometry of the dimer.²³ Allowing the two phenoxyl radicals to relax from this point to their equilibrium structures is downhill by 64.9 kcal mol⁻¹. Similar arguments and stabilization energies have been described by Scaiano and by Kochi and Head-Gordon for carbon-centered radical dimers.^{12,17} The calculated *vertical* bond energy of 74.3 kcal mol⁻¹ is only slightly larger than the bond energy predicted from Zavitsas' linear correlation (Figure 4A). The large stabilization energy is a result of the substantial structural difference between the dimer and monomer, particularly in the high frequency C–C and C–O bonds (Table 1).

The force constant of the central C-C bond of (***t***Bu₂OMeArO)₂ was obtained from the DFT calculations. Badger's rule relates bond lengths r_e to force constants k_e according to $r_e =$

$(C_{ij}/k_e)^{1/3} + d_{ij}$ where C_{ij} and d_{ij} are constants for a set of similar bonds.^{2,24} The Badger's rule plot in Figure 4B shows, remarkably, that the r_e, k_e pair falls right on the line formed by the values for simple hydrocarbons.

Thus the long bond length in (**^tBu₂OMeArO**)₂ correlates with the C–C bond force constant but not its bond dissociation enthalpy (BDE). Therefore the force constant does not correlate with the BDE. The bond length and force constant are both properties of the equilibrium structure of (**^tBu₂OMeArO**)₂ while the BDE also involves the energetics of the phenoxyl radical. The exceptionally weak C–C bond in (**^tBu₂OMeArO**)₂ – with a measured bond dissociation enthalpy of 6.1 kcal mol^{–1} – is due only in part to an intrinsically poor C–C bond. The C–C bond length of 1.6055(23) Å is longer than the typical 1.54 single bond distance, but is not long enough to explain the bond weakness. The low BDE is in large part due to be the substantial reorganization of the phenoxyl radical. This causes the substantial deviation from the suggested bond length/bond strength correlation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) Dissociation of $(^t\text{Bu}_2(\text{MeO})\text{ArO})_2$ dimer to $^t\text{Bu}_2(\text{MeO})\text{ArO}^\bullet$. (B) ORTEP of the X-ray crystal structure of the dimer.

Figure 2.

(A) IR transmittance spectrum of solid dimer (as a KBr pellet prepared in a glove box). (B) IR spectra of CCl₄ solutions of **Bu₂(MeO)ArO•** at 50 mM (black), 250 mM (red), and 500 mM (blue). The vertical axis is the absorbance divided by the [**Bu₂(MeO)ArO•**] in each solution, determined from the A(1292 cm⁻¹) (Figure S6).

Figure 3.

(A) Van't Hoff plot for dissociation of dimer. (B) UV-vis spectra of 10 μM (black) and 6 μM (red) **'Bu₂OMeArO•** in CCl₄ at 20 °C (solid line) and -20 °C (dashed line)

Figure 4.

(A) Plot of central C–C bond distances r (Å) vs. bond dissociation enthalpies (BDEs, kcal mol^{−1}), adapted from references¹ with data for $(^tBu_2OMeArO)_2$ added (red diamond). Experimental values from Zavitsas are shown as circles, with C_2H_6 , C_2H_4 , C_2H_2 highlighted as black circles;^{1a} triangles are calculated values;^{1b} blue circles and green triangles are from ¹² and ²¹. (B) Badger's rule plot for the C–C bonds in C_2H_6 , C_2H_4 , C_2H_2 , C_6H_6 (black

circles; experimental data²⁴) and the central C–C bond in (**^tBu₂OMeArO**)₂ (red diamond; experimental bond distance and calculated force constant (see SI).

Table 1

Comparison of crystallographic and calculated metrical data (Å, °) for (tBu₂(MeO)ArO)₂ and its monomer.

Bond	X-ray Structure	M06-2X/6-31+G(2d,2p)	
		dimer	monomer
C1-O1	1.2227(15)	1.215	1.244
C1-C2	1.5026(16)	1.503	1.470
C2-C3	1.3377(17)	1.335	1.378
C3-C4	1.4955(16)	1.497	1.403
C4-C5	1.4989(16)	1.497	1.411
C5-C6	1.3371(17)	1.335	1.367
C6-C1	1.5005(16)	1.503	1.474
C4-O2	1.4297(14)	1.413	1.342
C4-C4a	1.6055(23)	1.6065	-
Dihedral angle (C2,C3,C4,O2)	142.0	145.9	180.0