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A C−C Bonded Phenoxyl Radical Dimer with a Zero Bond Dissociation Free Energy

Jessica M. Wittman, Rebecca Hayoun, Werner Kaminsky, Michael K. Coggins, and James M. Mayer*

Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195-1700, United States

S *Supporting Information*

ABSTRACT: The 2,6-di-*tert*-butyl-4-methoxyphenoxyl radical is shown to dimerize in solution and in the solid state. The X-ray crystal structure of the dimer, the first for a para-coupled phenoxyl radical, revealed a bond length of 1.6055(23) Å for the C4−C4a bond. This is significantly longer than typical C−C bonds. Solution equilibrium studies using both optical and IR spectroscopies showed 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 gave an exceptionally small bond dissociation enthalpy (BDE) of 6.1 ± 0.5 kcal mol^{-1}. To our knowledge, this is the smallest 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 phenoxyl radical dimer with an extremely weak C−C bond.

Phenoxyl radicals are important in biology and natural and synthetic antioxidant chemistry, and they are increasingly being studied in radical and proton-coupled electron transfer (PCET) reactions.[5] Phenoxyl radicals that are protected at the 2-, 4-, and 6-positions, such as 2,6-di-*tert*-butyl-4-methoxyphenoxyl radical [$^t\mathbf{Bu_2(MeO)ArO}^\bullet$] are unusually stable in oxygen-free solutions.[6] In 1955, Müller and Ley found that the radical content of $^t\mathbf{Bu_2(MeO)ArO}^\bullet$ is not quantitative by magnetic susceptibility, and they proposed the equilibrium formation of the 4,4′-bis(cyclohexadienone) dimer $(^t\mathbf{Bu_2(MeO)ArO})_2$ (Figure 1A).[7] Reported here are the X-ray crystal structure and dissociation thermochemistry of this dimer.

$^t\mathbf{Bu_2(MeO)ArO}^\bullet$ 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 to form 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.

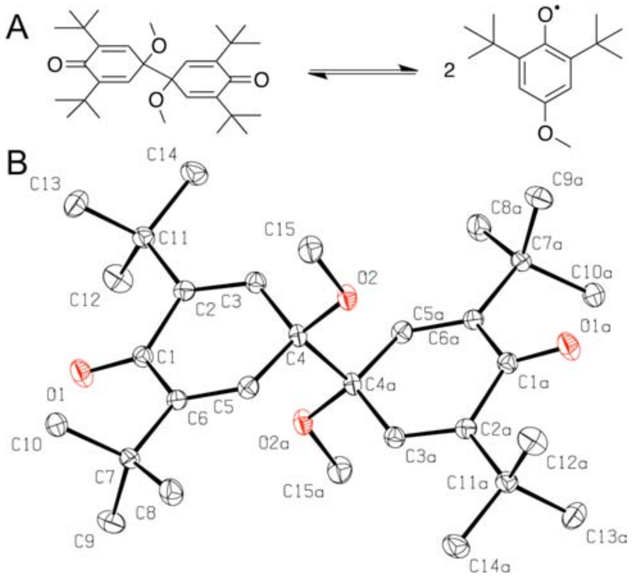

Figure 1. (A) Dissociation of $(^t\mathbf{Bu_2(MeO)ArO})_2$ dimer to give $^t\mathbf{Bu_2(MeO)ArO}^\bullet$. (B) ORTEP of the X-ray crystal structure of the dimer (H atoms omitted for clarity).

The metrical data for the structure of $(^t\mathbf{Bu_2(MeO)ArO})_2$ (Table 1) are consistent with the line structure in Figure 1A. The C1−O1 bond length of 1.2227(15) Å is characteristic of a C═O double bond. The C2−C3 and C5−C6 bond distances of 1.34 Å 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 C(sp^3)−C(sp^2) single bonds. The length of the C4−C4a bond connecting the two halves of the dimer is 1.6055(23) Å, which is much longer than the standard 1.54 Å C(sp^3)−C(sp^3) 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 to 1.64 Å.[11,12]

The bis(cyclohexadienone) structure was proposed by Müller and Ley on the basis of quinone-like stretches at ∼1600 and ∼1650 cm^{-1} in the solution IR spectrum of $^t\mathbf{Bu_2(MeO)ArO}^\bullet$.[7] An IR spectrum of our isolated solid dimer, prepared as a KBr pellet, shows two strong IR stretches at 1646 and 1667 cm^{-1} (Figure 2A).

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Table 1. Comparison of Crystallographic and Calculated Metrical Data for $({}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$ and Its Monomer

		M06-2X/6-31+G(2d,2p)	
bond/angle	X-ray structure	dimer	monomer
	Bond Lengths (Å)		
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 (deg)		
C2−C3−C4−O2	142.0	145.9	180.0

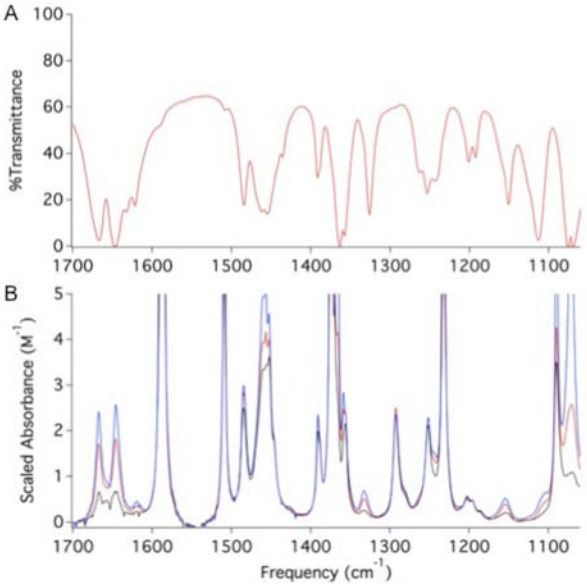

Figure 2. (A) IR transmittance spectrum of the solid dimer (as a KBr pellet prepared in a glovebox). (B) IR spectra of CCl_4 solutions of **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** at 50 mM (black), 250 mM (red), and 500 mM (blue). The vertical axis represents the absorbance divided by [**${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$**], as determined from the absorbance at 1292 cm^{-1} (Figure S6).

Density functional theory (DFT) calculations on the dimer at the M06-2X/6-31+G(2d,2p) level gave gas-phase bond lengths in close agreement with measured solid-state distances (Table 1).[13] The computed C4−C4a bond length of 1.6065 Å is within 3σ of the measured distance. The M06-2X functional was chosen because it accounts for long-range non-covalent 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 [Figure 2 and Figures S4 and S5 in the Supporting Information (SI)]. For instance, the C═O/C═C stretching frequencies were calculated to be 1629, 1660 (two modes), and 1690 cm^{-1}, versus the experimental values of 1622, 1632, 1646, and 1667 cm^{-1} both in the solid state (KBr pellet) and in solution (CCl_4) (Table S2 in the SI).

The equilibrium constant for dimer dissociation (K_{eq}) at 20 ± 2 °C was determined by solution IR spectroscopy in CCl_4. At low concentrations, only the monomer **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** was observed, while at ≥50 mM the dimer was evident from its bands at 1646 and 1667 cm^{-1} (Figure 2B). The concentration of **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** in solutions where both the 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 1A (Figure S8) gave $K_{\mathrm{eq}} = 1.3 \pm 0.2$ M at 20 °C. This corresponds to a free energy of -0.15 ± 0.1 kcal mol^{-1}.

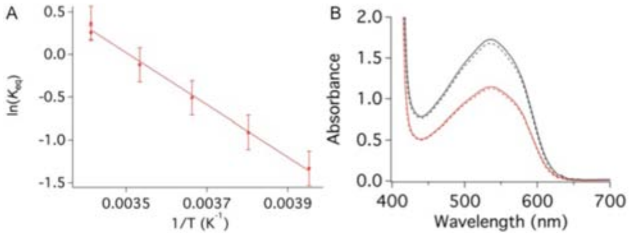

Figure 3. (A) Van't Hoff plot for dissociation of the dimer. (B) UV−vis spectra of 10 μM (black) and 6 μM (red) **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** in CCl_4 at 20 °C (solid line) and −20 °C (dashed line).

Equilibrium constants at temperatures from −20 to +20 °C were determined by measuring the optical absorbance of **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** in CCl_4 solutions (Figure 3B). For concentrated solutions, 1 or 2 mm path length cuvettes were used and the absorbance of **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** was measured at 605 nm rather than at the peak maximum. A plot of absorbance versus [**${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$**] for dilute (<20 mM) solutions of **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** at 22 ± 1 °C was linear with $\varepsilon = 44$ M^{-1} cm^{-1} at 605 nm (Figure S1). At concentrations above 20 mM and at lower temperatures, such Beer's Law plots were nonlinear, suggesting loss of **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** to form the dimer (Figure S2). The data were well-fit by the equilibrium in Figure 1A with the assumption of mass balance (Figure S3). The value of K_{eq} at 20 °C was found to be 1.4 ± 0.3 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 3A and Table S1) gave the enthalpy and entropy of dimer dissociation as $\Delta H° = 6.1 \pm 0.5$ kcal mol^{-1} and $\Delta S° = 21 \pm 1$ cal mol^{-1} K^{-1}.

$({}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$ 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 for which the BDE has been experimentally measured. The BDE is ≥8 kcal mol^{-1} smaller than the BDEs estimated by 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 and co-workers 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 $(4\text{-}{}^t\mathrm{BuPh})_3\mathrm{C}^{\bullet}$[19] and $2,4,6\text{-}{}^t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2\mathrm{O}^\bullet$ do not dimerize and therefore must form weaker C−C bonds than **${}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$**.

The C−C bond in **$({}^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$** is much weaker than would have been expected on the basis of 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

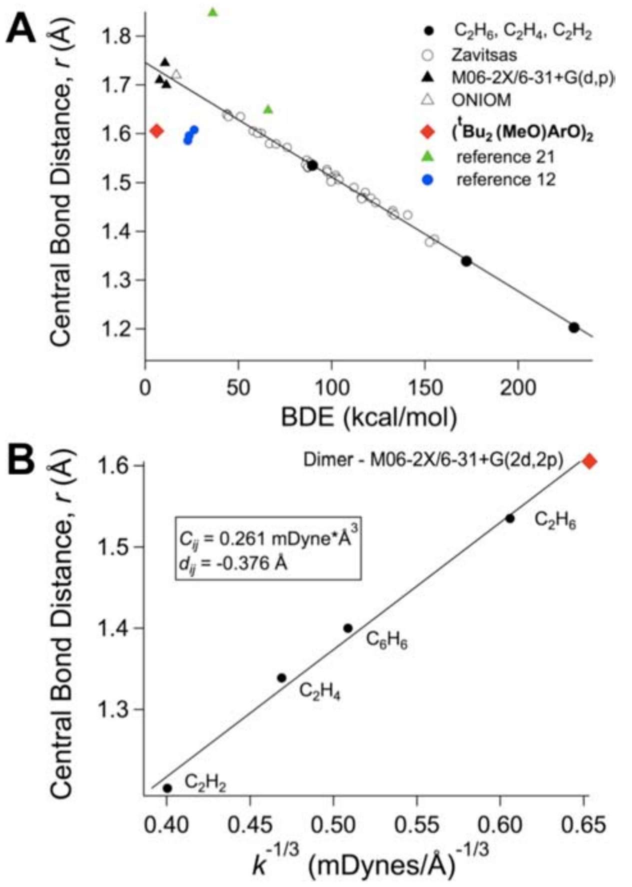

Figure 4. (A) Plot of central C−C bond distance (r) vs bond dissociation enthalpy (BDE), adapted from ref 1 with the data for **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$** added (red diamond). Experimental values from Zavitsas[1a] are shown as circles, with C_2H_6, C_2H_4, and C_2H_2 highlighted as black circles. Triangles are calculated values from ref 1b. Blue circles and green triangles show data taken from refs 12 and 21, respectively. (B) Badger's rule plot for the C−C bonds in C_2H_6, C_2H_4, C_2H_2, and C_6H_6 (black circles; experimental data[24]) and the central C−C bond in **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$** (red diamond; experimental bond distance and calculated force constant; see the SI).

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 data for Scaiano's C−C dimers are included in Figure 4A,[12] as are those for recently reported alkanes with long C−C bonds (up to 1.71 Å) but strong attractive dispersion forces, which deviate from the correlation in the opposite direction.[21]

The deviation of **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$** 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 **$^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO}^\bullet$** 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[12] and by Kochi and Head-Gordon[17] for carbon-centered radical dimers. 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 the monomer, particularly in the high-frequency C−C and C−O bonds (Table 1).

The force constant of the central C−C bond of **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$** 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] Remarkably, the Badger's rule plot in Figure 4B shows that the (r_e, k_e) pair for **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$** falls right on the line formed by the values for simple hydrocarbons.

Thus, the long bond length in **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$** correlates with the C−C bond force constant but not its BDE. Therefore, the force constant does not correlate with the BDE. Both the bond length and force constant are properties of the equilibrium structure of **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$**, while the BDE also involves the energetics of the phenoxyl radical. The exceptionally weak C−C bond in **$(^t\mathrm{Bu}_2(\mathrm{MeO})\mathrm{ArO})_2$**, with a measured BDE 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 single-bond distance of 1.54 Å but is not long enough to explain the bond weakness. The low BDE is in large part due to the substantial reorganization of the phenoxyl radical. This causes the substantial deviation from the suggested bond length/bond strength correlation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

mayer@chem.washington.edu

Notes

The authors declare no competing financial interest.

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