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Bond Dissociation Energies for Radical Dimers Derived from Highly Stabilized Carbon-Centered Radicals

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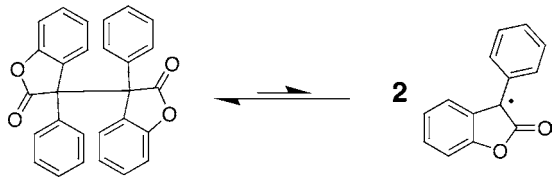
ABSTRACT



The temperature dependence of the dissociation of dimers formed from highly stabilized carbon-centered radicals has been examined. Analysis of the data yields the bond dissociation energy (BDE) for the central head-to-head C–C bond in these compounds. For example, for the dimer derived from 3-phenyl-2-coumaranone, BDE is 23.6 kcal/mol and the C–C bond length 1.596 Å, a rather long value for a σ bond.

Lactone-based antioxidants, introduced by Ciba a few years ago, have stimulated interest in the understanding of carbon-centered radicals with greatly attenuated reactivity toward oxygen.[1−5] We have proposed that the lack of reactivity toward oxygen can be rationalized on the basis of five parameters, all influential, but where their relative importance depends on the particular molecule under study. These parameters are as follows: (a) benzylic resonance stabilization; (b) favorable stereoelectronic effects, (c) unpaired spin delocalization on heteroatoms (particularly oxygen), (d) electron-withdrawing effects, and (e) steric effects.

Our recent studies have included lactones,[1,2] phthalides,[4] hydrocarbons,[5] and substituted nitriles.[3] Among these systems, radicals **1**−**4** (Figure 1) are either unreactive or have greatly attenuated reactivity toward oxygen, in contrast with the high reactivity of most carbon-centered radicals.[6,7]

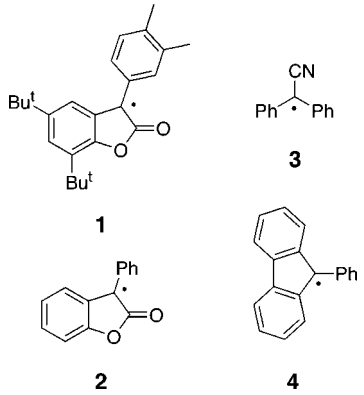


Figure 1. Structure of the radicals studied.

In radicals **1**−**4**, steric effects may contribute, but all indications are that they are not the dominant reason for the lack of reactivity toward oxygen. For example, all form head-

(1) Scaiano, J. C.; Martin, A.; Yap, G. P. A.; Ingold, K. U. *Org. Lett.* **2000**, *2*, 899−901.
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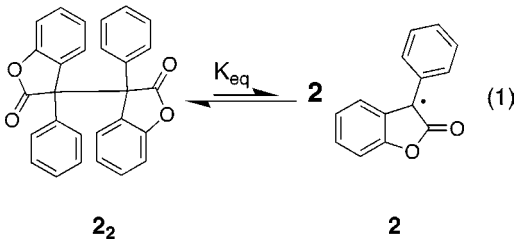
to-head dimers, a far more sterically demanding process than reaction with oxygen.

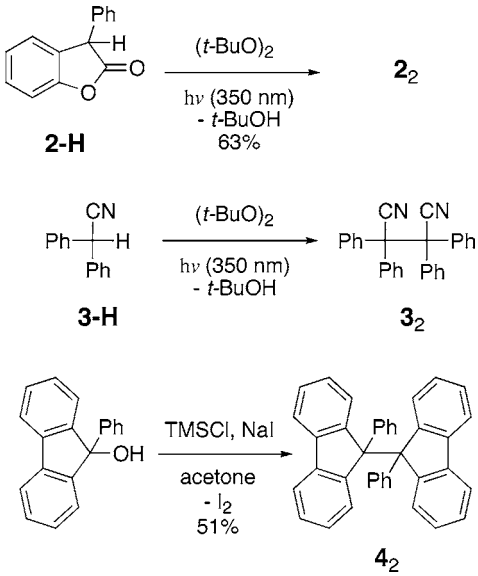
The other effects mentioned above play an important role, but their relative importance is strongly system-dependent. Thus, electron-withdrawing effects due to the lactone or nitrile moieties are important in **1**−**3**, but not in **4**. Stereoelectronic effects, leading to optimal geometry at the radical center assisted by the five-membered ring, are key to **1**, **2**, and **4**, but not for **3**. Heteroatom delocalization is important in **1** and **2** that possess some oxygen-centered character, while for **3** spin on nitrogen also leads to some C−CN double-bond character in the radical. Thus, while **1**−**4** all show attenuated or no reactivity toward oxygen, the parameters that control this lack of reactivity have very different weights in each system.

All radicals form head-to-head dimers, which at moderately high temperatures (vide infra) are present in solution in equilibrium with the radicals, as illustrated in eq 1 for radical **2**. Note also the nomenclature used for the dimers, simply adding the subscript "2" to the radical abbreviation.



Two novel synthetic methods are introduced for the formation of precursors to radicals **2**−**4** (Scheme 1). Dimers

Scheme 1. Synthetic Approach to Dimers $\mathbf{2_2}$, $\mathbf{3_2}$, and $\mathbf{4_2}$



$\mathbf{2_2}$ and $\mathbf{3_2}$ were obtained from the photolysis of *tert*-butyl peroxide at 350 nm in the presence of the corresponding monomeric substrate (**2-H** or **3-H**) under an inert atmosphere. While initial yields were mediocre, optimized conditions gave 63% of $\mathbf{2_2}$, a satisfactory outcome for the creation of such weakly bound dimers. A very convenient one-pot synthesis of $\mathbf{4_2}$ afforded 51% yield from the addition of 9-phenyl-9-fluorenol (**4a**) to stoichiometric TMS chloride and excess NaI in acetone followed by subsequent workup of released molecular iodine with 10% $Na_2S_2O_{3(aq)}$. The highly symmetric and practically insoluble $\mathbf{4_2}$ could be recovered from the filtration of a two-phase system of dichloromethane and aqueous $Na_2S_2O_3$.

Radicals **1**−**4** show significant and characteristic absorptions in the ultraviolet and visible regions. These absorptions can be used to monitor their presence in equilibria such as that illustrated in eq 1. At room temperature, the radical absorptions observed are negligible in comparison with their absorptions at the higher temperatures employed in our studies, and thus the room-temperature spectrum can be taken as a reference. It is noted that the absorbances of all samples were similar before and after the temperature-dependent experiments were conducted, indicating the reversibility of dimer formation. The temperature dependence of the spectra is shown in Figure 2 for dimer $\mathbf{1}_2$ in toluene.

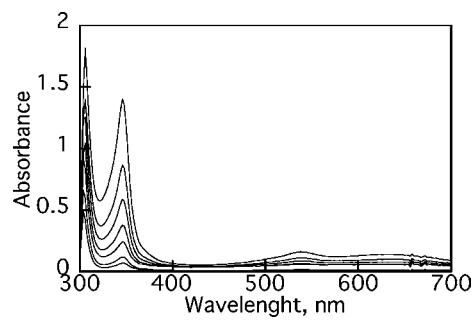


Figure 2. Absorption spectra of **1** at different temperatures, obtained by thermal dissociation of $\mathbf{1}_2$ in toluene under nitrogen.

We note that for dimers $\mathbf{1}_2$ and $\mathbf{2}_2$ where different diastereoisomers are possible, the crystal X-ray structures show that under our synthesis conditions (see the Supporting Information) only the meso isomer is produced.

Similar experiments to that shown in Figure 2 were carried out for the dimers using toluene as solvent (with the exception of dimer $\mathbf{4_2}$ carried out in 1,3-dichlorobenzene) and working under a nitrogen atmosphere. We note that in the case of **4** prolonged exposure to oxygen under conditions of thermal dissociation eventually leads to the formation of the peroxide, probably the result of trapping of a small concentration of peroxyl radicals by a large excess of the carbon-centered radical in an excellent example of the operation of the Fischer−Ingold persistent free-radical effect.[7,8]

The data obtained from the temperature dependence of the dissociation equilibria can be used to obtain the ΔH for

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Table 1. Bond Dissociation Energies and Central C−C Bond Length for Dimers of **1**−**4**

radical	monitored λ_{max} (nm)	temp range (°C)	C−C bond length (Å)	ΔH_{diss} (kcal mol^{-1})
1	346	48−111	1.586[a]	22.8
2	346	37−100	1.596[b]	23.6
3	336	48−102	1.608[c]	26.2
4	320	80−135		15.2

[a] From the crystal structure (see Figure S1, Supporting Information). [b] Reference 10. [c] Reference 11.

the process, which corresponds to the bond dissociation energy (BDE) for the central C−C bond. The data were analyzed using a simplified form of the van't Hoff equation, i.e.

$$\ln K_{eq} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

where $K_{eq} = [R]^2/[D]$, and R and D represent the radical and dimer, respectively. Using Beer's law, the experimental absorbance can be expressed as

$$A = \epsilon[R]l \quad (3)$$

Therefore, eq 2 converts to

$$\ln A = \frac{\ln(\epsilon^2 l^2 [D])}{2} + \frac{\Delta S}{2R} - \frac{\Delta H}{2RT} \quad (4)$$

Equation 4 shows that a plot of ln A against the reciprocal temperature will yield $-\Delta H/2R$ from the slope, provided that [D] can be approximated as constant throughout the temperature range studied. This criterion is easily met by the systems under study. For example, in the case of $\mathbf{1}_2$ (see Figure 1), the absorbance at 111 °C (the highest temperature used) is approximately 1.4 for an optical path of 1 cm; [D] = 0.01 M and the use of a previously reported method[9] estimated a radical extinction coefficient of 37 500 M^{-1} cm^{-1} at 346 nm. From this we evaluate a radical concentration of 3.7×10^{-5} M, or a dimer conversion of ∼ 0.19%, low enough to assume that [D] is constant. Thus, under these conditions it is not necessary to know the absolute value of the radical extinction coefficients, which are frequently subject to considerable uncertainty.

Figure 3 shows the plots according to eq 4 for dimers of **1**−**4**, from which the corresponding BDE were estimated and are listed in Table 1.

While all plots gave excellent correlation, with statistical errors around 0.1 kcal/mol, we estimate that the true uncertainty of the BDE values is probably ±0.5 kcal/mol.

We also took advantage of the availability of an estimated extinction coefficient for **1** in order to estimate the entropy

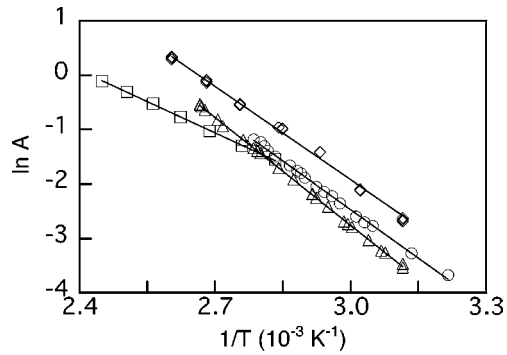

Figure 3. Van't Hoff plot according to eq 4 for dimer $\mathbf{1_2}$ (◇), $\mathbf{2_2}$ (○), and $\mathbf{3_2}$ (△) in toluene and $\mathbf{4_2}$ (□) in 1,3-dichlorobenzene under nitrogen.

change for the dissociation of $\mathbf{1_2}$. From the intercept obtained from the plot according to eq 4 we were able to estimate ΔS ∼ +28 gibbs/mol, a very reasonable value for a dissociation of this type.

The BDE found for $\mathbf{1}_2$ and $\mathbf{2}_2$ are very similar, showing that the presence of alkyl groups in **1** does not play an important role in controlling the stability of the radical generated. In an attempt to provide more evidence to explain this behavior, we obtained the X-ray structure for dimer $\mathbf{1_2}$ (Figure S1, Supporting Information) and compared it with that reported for 3-phenyl-2-coumaranone dimer $\mathbf{2_2}$. In both molecules the phenyl groups adopt a gauche conformation to decrease the repulsion between the carbonyl groups; however, the *tert*-butyl groups in **1** are oriented toward the exterior of the molecule to minimize steric interactions near the central bond. It is clear that in all cases the central C−C bond is much longer than the typical 1.54 Å for single bonds between sp^3 carbons. The C−C bond dissociation energies in these dimers are remarkably low; compare for example with AIBN, a typical initiator for free radical polymerization that decomposes with an activation energy of 31.3 kcal/mol and is usually regarded as an unstable compound.[12] While the radicals possess significant resonance stabilization, this is not enough to prevent their dimerization, and in this sense tha radicals are not persistent. The apparent stability of the dimers in Table 1 is probably due to the intrinsic lack of reactivity of the radicals with oxygen, that makes the back reaction to reform the dimer the preferred reaction path for the radicals; thus, while the dimers are stable compounds at room temperature, their stability reflects the tendency of any radicals formed to recombine. The compounds are best described as "*dynamically stable*".

Finally, we note that while the dimers studied in this contribution all show simple mechanistic behavior, with head-to-head dimer formation, other systems may show a

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preference for coupling at other positions in the ring, just as triphenylmethyl radical does. In dimers $\mathbf{1}_2-\mathbf{4}_2$ the BDE values support the arguments about the high degree of radical stabilization proposed earlier on the basis of their interactions (or lack thereof) with oxygen and the excellent hydrogen donor properties of their H-saturated precursors. With their weak bonds, high radical stability, and inertness toward oxygen, these dimers are promising compounds in the potential generation of thermomagnetic or photomagnetic materials.

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Supporting Information Available: Experimental details for the temperature-dependent measurements and for the synthesis of dimers $\mathbf{1_2}$, $\mathbf{2_2}$, $\mathbf{3_2}$, and $\mathbf{4_2}$. ORTEP diagram for $\mathbf{1_2}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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