JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Cite This: *J. Am. Chem. Soc.* 2019, 141, 12901−12906

pubs.acs.org/JACS

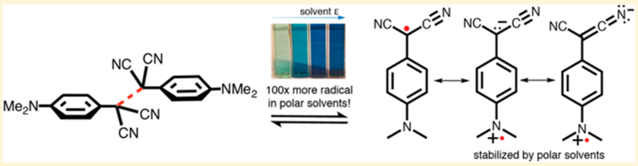
Solvent Effects on the Stability and Delocalization of Aryl Dicyanomethyl Radicals: The Captodative Effect Revisited

Joshua P. Peterson and Arthur H. Winter*

Department of Chemistry, Iowa State University, 1608 Gilman Hall, Ames, Iowa 50010, United States

Supporting Information

ABSTRACT: The captodative effect postulates that radicals substituted with both electron donating and accepting groups enjoy a special enhanced stabilization, a model given theoretical support by simple MO and resonance arguments. A key prediction from theory is that captodative stabilization of radicals is larger in polar solvents than in nonpolar solvents or the gas phase, which can be viewed in the resonance model as solvent stabilization of charge-separated resonance forms. Yet, several experimental studies have failed to observe a solvent effect on radical stability, casting doubt on key aspects of the captodative effect. Here, we examine in detail the effect of solvent on the stability of structurally related captodative aryl dicyanomethyl radicals. An attractive feature of these radicals is that they exist as stable steady state populations of radicals in equilibrium with their dimers, allowing us to directly characterize from experiment their thermodynamic stabilities and spin delocalization in solvents of varying polarity. In contrast to the prior studies, we find that captodative radicals are indeed stabilized by polar solvents, as measured by a shift in the radical−dimer association constants by up to 100-fold toward the radical upon going from nonpolar toluene to more polar DMF. Moreover, in polar solvents, the spin is shifted onto the donor substituent and away from the benzylic carbon. Within the resonance model, these results can be explained by the increased contributions of the zwitterionic resonance structures to the overall hybrid. These results provide experimental support to a key prediction from theory that had previously been dismissed.



INTRODUCTION

Radicals substituted with both donor and acceptor groups have been postulated to be specially stabilized and are termed captodative radicals (or merostabilized or push−pull radicals). The effect was hinted at by Dewar in the early 1950s[1] and subsequently investigated in more detail by Viehe and others.[2] From simple MO models, interactions of radicals with either neighboring donor groups or acceptor groups are stabilizing, and the combination of both donors and acceptors is further stabilized[3] (see Figure 1).

Within the resonance model, radicals featuring both donors and acceptors have additional charge-separated resonance structures that radicals substituted either with multiple donors or multiple acceptors do not. These additional resonance structures hint at the possibility of cooperative stabilizing effects enjoyed by radicals featuring both donors and acceptors. Evidence both for[4,5] and against[6−8] the captodative effect has been presented, and while there is some agreement on the existence of the captodative effect in a general sense, like other conceptual models such as aromaticity, there is little agreement on the magnitude of the effect and its importance for specific radicals.

A particularly interesting prediction from early theoretical work by Katritzy and coworkers[9] was that captodative stabilization should be large in high-dielectric solvents but minimal in low dielectric solvents, leading them to call the captodative phenomenon “mostly a solvent effect”.[10] These predictions are easily understood from the resonance model by solvent screening of the unique charge-separated resonance structures that exist only for radicals bearing both donor and acceptor substituents. However, subsequent experimental work by Beckhaus and Rüchardt[11] showed no solvent dependence on the barriers for dissociation of alkoxy cyanomethyl radical homodimers into the free radicals, providing “unequivocal evidence in *disfavor* of the postulated increase in the “merostabilization” by polar solvents” for these radicals (emphasis added). A later study by Rhodes and Roduner[12] on cyclohexadienyl radicals containing both donor and acceptor groups also “argued against the prediction that a highly polar medium has a significant promoting influence on the captodative phenomenon”. A study by Viehe and coworkers[13] on E/Z isomerization of cyclopropane derivatives proceeding through captodative diradicals found no solvent effect on the free energy barriers. These experiments have cast doubt on key aspects of the captodative effect. One can reasonably ask, if there is no solvent stabilization of the radicals, as would be expected from the charge-separated resonance structures and theory, is there a cooperative captodative effect at all?

Here, we examine the effect of solvent on the stability of structurally related captodative aryl dicyanomethyl radicals. These radicals have seen recent interest upon Seki and coworkers’ discovery[14−16] that a *para* substituent on the aryl group blocks an irreversible head-to-tail dimerization, leading to

Received: June 20, 2019
Published: July 28, 2019

DOI: 10.1021/jacs.9b06576
J. Am. Chem. Soc. 2019, 141, 12901−12906

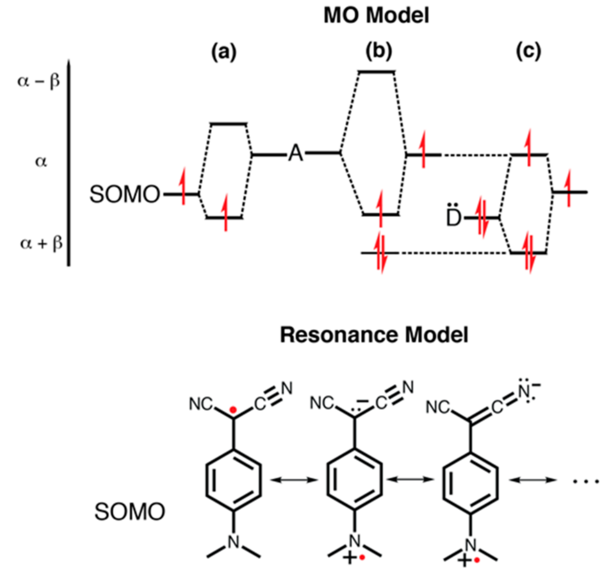


Figure 1. (Top) MO model for the captodative effect,[3,4] showing the stabilization of a radical with an electron acceptor (a), an electron donor (c), and the combined effect (b). (Bottom) Resonance model depicting zwitterionic structures unique to captodative radicals.

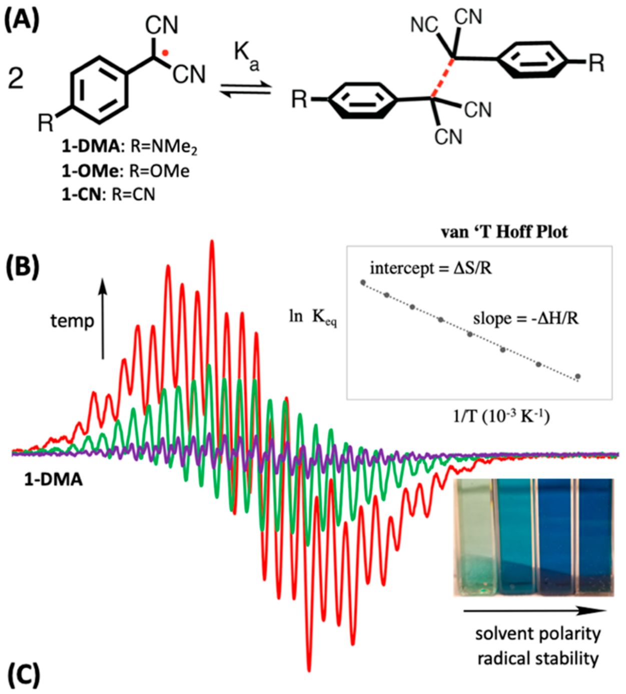
air and thermally stable steady state populations of radicals that can be directly detected by electron paramagnetic resonance (EPR) spectroscopy. Because these radicals can be directly detected rather than existing as fleeting intermediates, we were able to evaluate the effect of solvent on their stability and radical delocalization using direct measurements. We measured the equilibrium constants of the radical with its dimer in solvents of varying polarity to probe relative radical stabilities as a function of solvent dielectric constant and as a function of the donating ability of the aryl ring. We also measured the change in the spin densities as a function of solvent by measuring EPR hyperfine coupling constants.

We find that, in contrast to the work of Beckhaus and Rüchardt and Rhodes and Roduner, polar solvents do indeed stabilize these radicals, as shown by a change in the radical−dimer association constant by ∼100-fold for radicals bearing a strong donating group upon changing from nonpolar to polar solvents, an effect whose magnitude is directly correlated to the strength of the donating aryl ring. Furthermore, we observe the increased delocalization of the radical in polar solvents by changes in the EPR hyperfine coupling as solvent polarity is increased, providing experimental evidence in favor of the theoretical prediction that polar solvents can stabilize captodative radicals, a claim that was thought to be discredited.

■ RESULTS AND DISCUSSION

Solvent Effects on the Radical−Dimer Equilibrium Constants. Aryl dicyanomethyl radicals containing a very strong donating group (*para*-dimethylamino, **1-DMA**), a less strong donating group (*para*-methoxy, **1-OMe**), and a withdrawing group (*para*-cyano, **1-CN**) were prepared by oxidation of the corresponding aryl malononitriles by known methods.[17,18] These paramagnetic radicals exist in equilibrium with their diamagnetic EPR-silent dimers.

To evaluate the effect of solvent on the stability of these radicals, we determined the association constant, K_a, for dimerization of each of these radicals in varying solvents as an indicator of relative radical stability. Association constants for radical dimerization were determined by EPR spectroscopy using van't Hoff plots (example shown in Figure 2B; all others are included in the Supporting Information). Given that we are modifying the *para* position distant from the C−C bond, changing the substituents is anticipated to have a negligible steric effect on the dimer stability, so the radical−dimer equilibrium constant is a useful experimental probe of relative radical stability.



(C)

R	K_a (M^{-1}), toluene	K_a (M^{-1}), DMF
CN	1.8×10^8	1.6×10^8
OMe	4.5×10^6	1.6×10^6
NMe_2	2.0×10^5	2.5×10^3

Figure 2. (A) Radical/dimer equilibrium for dicyanomethyl systems; (B) example VT-EPR with van't Hoff plot insert for **1-NMe$_2$**; (C) binding data of representative compounds in a nonpolar (toluene) and polar (DMF) solvent.

In contrast to the prior work, we observe a significant solvent effect on radical stability with strong donors. The simple resonance model predicts that captodative radicals should be stabilized in polar solvents due to screening of the unique charge-separated resonance structures that exist only for captodative radicals. Indeed, that is what we observe experimentally. For the very strongly donating *p*-dimethylamino-phenyl-substituted radical, **1-DMA**, we observe a remarkable ∼100-fold change in the association constant upon going from nonpolar toluene to more polar DMF (2.0×10^5 to 2.5×10^3 M^{-1}) in favor of the radical (see Figure 2C). The shift in the equilibrium toward the radical is also readily apparent simply from visual inspection of solutions of these radicals in solvents of varying polarity, which are dark blue in polar solvents, indicating large amounts of the colored radical, and faintly blue in nonpolar solvents, indicating mostly uncolored dimer (inset in Figure 2B).

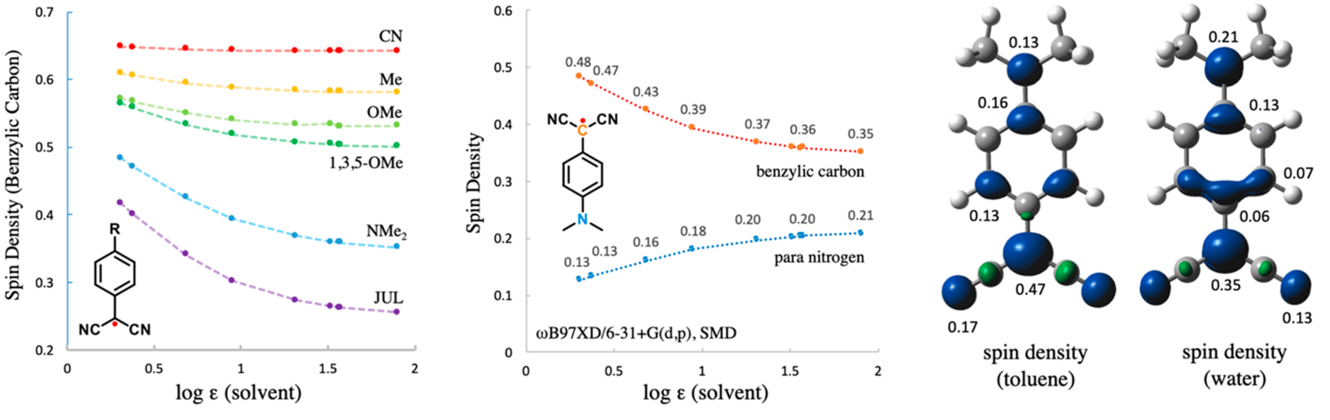


Figure 3. Computed Mulliken spin densities (*ω*B97XD,6-31+G(d,p), SMD) on the benzylic carbon of differently substituted dicyanomethyl radicals in solvents of varying dielectric (left); spin density comparison of the benzylic carbon and *para* nitrogen in the NMe_2 radical system as a function of solvent dielectric (center); spin density distributions across **1-DMA** in a nonpolar and polar solvent (right). JUL = julolidine.

With the less donating *p*-methoxyphenyl-substituted radical, **1-OMe**, the association constant is an order of magnitude larger than that for **1-DMA** in toluene, indicating less radical stability. Moreover, the solvent effect on the equilibrium is drastically diminished with a change in K_a of only ∼3-fold (4.5×10^6 to 1.6×10^6 M^{-1} in toluene and DMF, respectively). Thus, **1-OMe** and **1-DMA** are an order of magnitude apart in equilibrium constant in toluene but three orders of magnitude in polar DMF, where **1-DMA** radical is strongly stabilized by solvent, while **1-OMe** is less stabilized. With the withdrawing *p*-cyanophenyl-substituted radical, **1-CN**, which is no longer a captodative radical, the association constant is larger by two orders of magnitude than **1-OMe** in toluene, indicating further diminished radical stability. For this radical, effectively no solvent effect on radical stability is observed (1.8×10^8 to 1.6×10^8 M^{-1} in toluene and DMF, respectively). These studies indicate that radicals substituted with very strong polarizable donors with strong acceptors have large solvent effects on radical stability. The solvent effect is drastically attenuated by substituting a very strong donor (e.g., Me_2N) with merely a strong donor (e.g., OMe) and is negligible with a withdrawing group.

Computational and Experimental Evaluation of Spin Delocalization as a Function of Solvent Dielectric. The simple resonance model suggests that, in polar solvents, radical stability increases due to solvent screening of zwitterionic resonance structures. If this is true, then the rationalization for the enhanced stability of **1-DMA** in polar solvents is radical delocalization. The prediction, then, is that spin density should shift from the benzylic carbon to the donating substituent in the *para* position in more polar solvents, as the zwitterionic resonance structures contribute more to the overall hybrid. All of the zwitterionic resonance structures feature spin sites that are delocalized off of the benzylic carbon (see Figure 2A).

To test this prediction, we computationally evaluated the spin densities of a series of radicals bearing varying substituents using density functional theory (*ω*B97XD,6-31+G(d,p)) and in solvents of varying dielectric using the SMD solvation model (see Figure 3). From these computations, the spin density on the benzylic carbon decreases as the aryl substituent becomes more donating. Furthermore, the change in the spin density on the benzylic carbon as the solvent polarity is largest with strong donating groups, modest with less strong donors, and nonexistent with withdrawing groups. Figure 3 (middle) shows the spin density on the dimethylamino substituted radical, **1-DMA**, as solvent polarity is increased. In toluene, the computed (Mulliken) spin density on the benzylic carbon is 0.47, while in water, the spin density decreases to 0.35. Concomitantly, the spin density on the dimethylamino nitrogen increases from 0.13 to 0.21 upon changing solvent from toluene to water. This computational result supports the idea of increased contribution of zwitterionic resonance structures to the hybrid in polar solvents, which rationalizes the increased radical stability in polar solvents.

We also evaluated spin densities experimentally using the EPR hyperfine coupling constants for these radicals. Estimates of the spin densities for planar π radicals can be obtained from the McConnell equation,[19] where the hyperfine coupling constant to spin-active nuclei is directly proportional to the spin density, following the equation $A = Q\rho$, where A is the hyperfine coupling constant, ρ is the pi spin density, and Q is the McConnell constant (∼22 for planar carbon pi radicals[20]). The EPR spectrum for the *p*-dimethylaminophenyl dicyanomethyl radical, **1-DMA**, is shown in toluene, dichloromethane, and acetone in Figure 4. The hyperfine coupling varies as a function of solvent, indicating changes in spin density for this radical as a function of solvent. We found that the *para*-nitrogen Mulliken spin density from computation correlates strongly with spin densities estimated from computed A values and using the McConnell equation ($Q = 22$). The Mulliken spin densities for toluene,

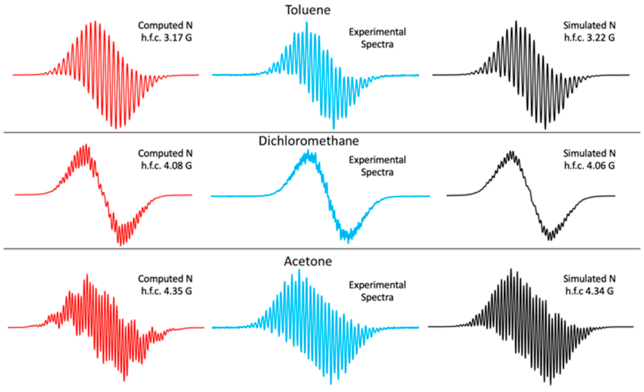


Figure 4. Computed (left) EPR spectra using the computed A hyperfine coupling (h.f.c.) values from (B3LYP/EPR-III, SMD) compared to experimental EPR spectra (middle) and simulated values for the **1-NMe_2** radical.

dichloromethane, and acetone were computed to be 0.14, 0.18, and 0.20, respectively. Using the McConnell equation with computed *G* values, the spin densities were calculated to be 0.14, 0.19, and 0.20 for toluene, dichloromethane, and acetone, respectively.

The EPR spectrum simulated directly from the *A* values predicted by computation (B3LYP/EPR-III, SMD) without modification is shown to the left of the experimentally obtained spectrum, which shows surprisingly reasonable agreement. A purely simulated spectrum to best match the experimental spectrum is shown to the right. In the case of toluene, the computed nitrogen *A* value is 3.2 G, while in acetone, it is 4.4 G, indicating an increase in spin density onto the substituent as the solvent polarity is increased. In contrast, the computed ^{13}C hyperfine coupling constant for the benzylic carbon decreases from 11.6 gauss to 8.6 gauss, indicating delocalization off the benzylic carbon with increasing solvent polarity. We also simulated the EPR spectra by adjusting the *A* values to best match the experimental spectra. Only small variations in the computed *A* values led to good fits (see Figure 4).

These results provide a rationalization for the dimerization equilibrium measurements above, which indicate that the captodative effect is largest with strong donating groups and polar solvents and requires highly polarizable radicals and polar solvents for maximal effect. In more polar solvents, the radical is stabilized by additional delocalization off of the benzylic carbon and onto the donating substituent.

Benzylic Carbon Spin Density as a Proxy for Radical Stability. Our results above suggest an inverse correlation between the amount of spin density on the benzylic carbon and radical stability. To evaluate the nature of this correlation, we plotted the experimentally determined association constants on a log scale vs the DFT-predicted spin density on the benzylic carbon (ωB97XD,6-31+G(d,p), SMD). The results are shown in Figure 5. A striking correlation is observed, suggesting that radical delocalization may be useful as a direct proxy for radical stability. The trend shows that the less computed spin density on the benzylic carbon, the more radical is observed experimentally in the radical−dimer equilibrium. That is, radicals with more spin delocalization are more stable. Furthermore, this correlation may allow the estimation of radical dimerization binding constants simply by computing the spin density on the benzylic carbon of the free radical without computing the dimer, which may prove to be highly useful as the dimer is notoriously difficult to model accurately (having a C−C bond length >1.6 Å), requiring expensive computational methods with high levels of correlation.

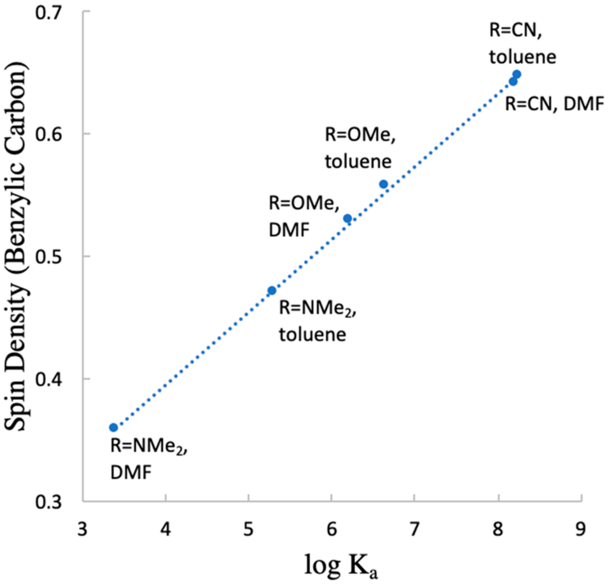


Figure 5. Plot of computed spin density on the benzylic carbon versus the experimentally derived binding constants on a log scale.

Effect of Solvent on Radical Geometries and Atomic Charges. In addition to changing spin densities of captodative radicals, we considered the possibility that the molecular geometries of the radicals might change in solvents of varying polarity due to the electronic reorganization of the radical as the solvent polarity is increased. In more polar solvents, as more zwitterionic character is incorporated into the electronic hybrid, the molecular geometries would be expected to change. Thus, we evaluated the computed geometries for **1-DMA** and **1-CN** in toluene and DMF using the SMD solvation model. Select bond lengths are shown in Figure 6. Surprisingly, there are few geometric effects in the solvents of large difference in polarity. For **1-CN**, the geometries are effectively identical, which is not surprising given that this is not a captodative radical, but with **1-DMA**, there is only a tiny decrease in the length of the C−N bond (by ∼0.01 Å). This is surprising because if greater zwitterionic character is mixing into the overall hybrid, the geometry would be expected to change more toward that of a zwitterion geometry. In the zwitterionic resonance form, the nitrogen takes on radical cation character, and the benzylic carbon takes on anion character. However, through examination of the geometry of the dimethylanilinium radical cation (Figure 6, right), it can be seen that the C−N bond and the adjacent C−C ring bonds are effectively the same as those for the radical in the gas phase. This result suggests that the lack of geometric change of the radical upon increasing the solvent polarity is due to the zwitterionic form having essentially the same preferred geometry as that of the neutral radical.

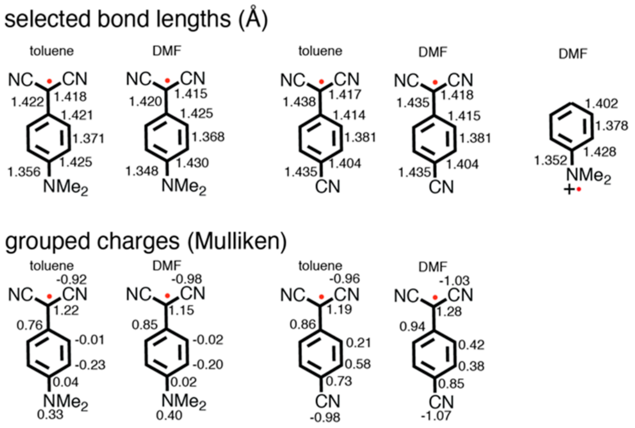


Figure 6. (Top) Select bond lengths (Å) for **1-DMA** and **1-CN** in toluene and DMF (ωB97XD/6-31+G(d,p), SMD). Dimethylaniline radical cation is shown as a reference. (Bottom) Grouped Mulliken atomic charges for **1-DMA** and **1-CN** in toluene and DMF (ωB97XD/6-31+G(d,p), SMD).

The computed Mulliken atomic charges provide more convincing evidence of the increased contribution of zwitterionic character into **1-DMA** in polar solvents (Figure 6, bottom). Upon going from toluene to DMF, the dicyanomethyl group becomes more negative by 0.19 charge units. Concomitantly, the dimethylamino group becomes more positive by 0.07 charge units. This result is suggestive of increased contribution of charge separated resonance structures. In contrast, for **1-CN**, which is not a captodative radical, the charges change slightly upon going from toluene to DMF, but in the other direction (e.g., the dicyanomethyl group becomes more positive).

Investigating the Failure of Prior Studies to Identify a Solvent Effect on the Stability of Captodative Radicals. The radicals featured in the two major studies[11,12] failing to observe a solvent effect on the stability of captodative radicals are shown in Figure 7. We computationally evaluated the effect of solvent on the spin densities for these radicals and find that, in contrast to **1-DMA** described here, these radicals show little change in spin density as a function of solvent dielectric constant, indicating that no solvent effect is expected. Given that these previously studied radicals featured donors not as strong as NMe_2 (e.g., OMe), and that we have shown here that very strong donors are required to see a significant solvent effect, we evaluated computationally what would happen if very strong donor groups (e.g., NMe_2) would have been chosen along with an extra withdrawing nitrile group. The results are shown in Figure 7 (bottom). In these cases, a significant change in the spin density is predicted for these alternative radicals as a function of the solvent polarity, suggesting that the two prior studies unluckily chose insufficiently strong donors and acceptors to observe a solvent effect. A solvent effect would be expected for these proposed derivatives.

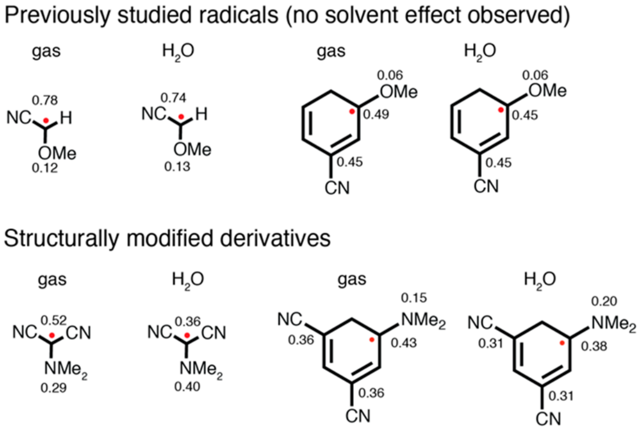


Figure 7. Plot of select computed Mulliken spin density (ωB97XD,6-31+G(d,p), SMD) for the radicals showing no captodative solvent effect (top) in water and gas phase and modified structures with stronger donors and another acceptor, showing a larger solvent effect.

COMPUTATIONAL METHODS

All compounds were initially optimized at the UωB97XD/6-31+G-(d,p) level of theory[21] using Gaussian16[22] using the SMD solvation model.[23] This functional and basis set were previously determined to be accurate and suitable for investigating dicyanomethyl radicals.[17,18,24] The Mulliken spin density population scheme was used to determine how the spin density throughout the pi-system varies with solvent for different compounds (other population schemes are available, but we are interested mostly in changes in spin density, for which the Mulliken population scheme is suitable). For the computation of hyperfine coupling values for the NMe_2 radical across all solvents, we used the B3LyP/EPR-III level of theory.[25,26]

EXPERIMENTAL METHODS

Binding Constants and van't Hoff Plots. To obtain the binding constants for the radical−dimer equilibria, the EPR spectrum of the dissolved radicals were recorded to determine the equilibrium constant between the radical and dimer at varying temperatures. To determine the equilibrium constants, the amount of radical at each temperature was quantified by double integration of the EPR signal (an example is shown in Figure 2B). From a van't Hoff plot (ln K_{eq} vs $1/T$, Figure 2B, inset), all of the equilibrium parameters ($\Delta H°$ and $\Delta S°$, and subsequently $\Delta G°$ and K_a) were obtained. All van't Hoff plots in all solvents are shown in the Supporting Information. Radical/dimers were obtained by quantitative oxidation of arylmalononitrile C−H precursors as described previously.[18,19]

Radical Generation. Following the synthesis previously published in our group, a fresh sample of each radical precursor compound was synthesized by palladium-catalyzed cross coupling from the starting aryl bromide. After purification by column chromatography (80:20 hexanes:EtOAc), pure compounds were dissolved into the solvent of study, and a 10-fold excess of PbO_2 was added to the mixture. After 30 min of stirring, the samples were centrifuged multiple times until all of the lead oxidant was removed from the solution. The resulting radicals in solution were then purged with nitrogen gas and added to prepurged quartz EPR tubes.

EPR Measurements. After the oxidation and preparation of radicals into EPR tubes, the following measurements were performed under the following settings. All samples were allowed to equilibrate for 5 min at each temperature before running a scan. A minimum of 8 scans were recorded at each temperature point; more scans were sometimes necessary for samples with low radical content. Solutions of toluene allowed the use of 3 mm quartz EPR tubes while all other solvents needed a specially designed 1 mm quartz EPR tube due to the higher dielectric constant of the solvent. The instrument parameters were set as follows: modulation frequency, 100 kHz; receiver gain, 50 dB; modulation amplitude, 0.5 G; time constant, 0.01 s; center field, 3335 G; sweep width, 150 G; microwave attenuation, 20 dB; microwave power, 2 mW; number of data points, 2048.

CONCLUSIONS

In summary, we demonstrated that for captodative radicals bearing very strong polarizable donors and acceptors, radical stability is solvent dependent. Within polar solvents, the radical is stabilized, which can be rationalized by increased contributions from zwitterionic canonical structures within the resonance model. This model is supported by increased spin delocalization in polar solvents, the change in the computed atomic charges in different solvents, and the correlation of the benzylic carbon radical spin density and the radical−dimer equilibrium constant. Although the theoretical predictions by Katritzky and coworkers[10,12] appear to be wrong for specific cases, and their claim that the captodative stabilization is "mostly a solvent effect" is highly suspect, the previous experimental studies that dismissed the importance of solvent stabilization on captodative radicals appear to have unluckily chosen example radicals substituted with insufficiently polarizable donors and acceptors. Had they studied slight structural variants, our computations (Figure 7) indicate that a solvent effect may have been observed. It is important to note that the concept of polarizability is fundamental to the captodative effect and has far-reaching consequences that extend to the reactivity of radicals and diradicals. On the basis of this work, we conclude that Katritzky and coworkers' general prediction that polar solvents can stabilize captodative radicals was correct, vindicating a key prediction from theory.

DOI: 10.1021/jacs.9b06576
J. Am. Chem. Soc. 2019, 141, 12901−12906

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b06576.

Computational Cartesian coordinates and SMD model spin delocalizations, UV−vis spectra, and van't Hoff plots (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: winter@iastate.edu.

ORCID

Joshua P. Peterson: 0000-0002-9897-238X

Arthur H. Winter: 0000-0003-2421-5578

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Iowa State Chemical Instrumentation Facility, specifically Dr. Sarah Cady, for EPR guidance. We thank the National Science Foundation (NSF) (CHE-1464956) and the Bailey Research Award for financial support. We also thank HPC@ISU for equipment use at Iowa State University, some of which was purchased through funding provided by the NSF under MRI Grant CBS 1229081 and CRI Grant1205413.

■ REFERENCES

(1) Dewar, M. J. S. A Molecular Orbital Theory of Organic Chemsitry. IV. Free Radicals. *J. Am. Chem. Soc.* **1952**, *74*, 3353.

(2) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. The captodative effect. *Acc. Chem. Res.* **1985**, *18* (5), 148−154.

(3) Klessinger, M. Captodative Substituent Effects and the Chromophoric System of Indigo. *Angew. Chem., Int. Ed. Engl.* **1980**, *19* (11), 908−909.

(4) Crans, D.; Clark, T.; von Ragué Schleyer, P. A theoretical evaluation of the synergetic capto-dative stabilisation of free radicals. *Tetrahedron Lett.* **1980**, *21* (38), 3681−3684.

(5) Baldock, R. W.; Hudson, P.; Katritzky, A. R.; Soti, F. Stable free radicals. Part I. A new principle governing the stability of organic free radicals. *J. Chem. Soc., Perkin Trans. 1* **1974**, No. 0, 1422−1427.

(6) Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. A Theoretical Approach to Substituent Effects in Radical Chemistry. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; Springer: Dordrecht, Netherlands, 1986; pp 1−48.

(7) Pasto, D. J. Radical stabilization energies of disubstituted methyl radicals. A detailed theoretical analysis of the captodative effect. *J. Am. Chem. Soc.* **1988**, *110* (24), 8164−8175.

(8) Viehe, H. G.; Janousek, Z.; Merényi, R. *Substituent Effects in Radical Chemistry*; Springer: Netherlands, 2012.

(9) Korth, H.-G.; Sustmann, R.; Merényi, R.; Viehe, H. G. Absolute rates for dimerization of capto-dative substituted methyl radicals in solution: absence of kinetic stabilization. *J. Chem. Soc., Perkin Trans. 2* **1983**, No. 1, 67−74.

(10) Katritzky, A. R.; Zerner, M. C.; Karelson, M. M. A quantitative assessment of the merostabilization energy of carbon-centered radicals. *J. Am. Chem. Soc.* **1986**, *108* (23), 7213−7214.

(11) Karelson, M.; Tamm, T.; Katritzky, A. R.; Szafran, M.; Zerner, M. C. Reaction Field Effects on the Electronic Structure of Carbon Radical and Ionic Centers. *Int. J. Quantum Chem.* **1990**, *37*, 1−13.

(12) Beckhaus, H.-D.; Rüchardt, C. The Effect of Solvent on the Stability of mero-Substituted Alkyl Radicals. *Angew. Chem., Int. Ed. Engl.* **1987**, *26* (8), 770−771.

(13) Rhodes, C. J.; Roduner, E. Muon Spin Rotation Studies of the Role of Solvent in Captodative Interactions of Cyclohexadienyl Radicals. *Hyperfine Interact.* **1991**, *65*, 975−978.

(14) Merényi, R.; Janousek, Z.; Viehe, H. G. Studies on the Captodative Effect. Entropy/Enthalpy Compensation as Solvent Effect in Radical Forming Reactions. A Relative Radical Stabilisation Scale. In *Substituent Effects in Radical Chemistry*; Viehe, H. G.; Janousek, Z., Merényi, R., Eds.; Springer: Dordrecht, Netherlands, 1986; pp 301−324.

(15) Kobashi, T.; Sakamaki, D.; Seki, S. N-Substituted Dicyanomethylphenyl Radicals: Dynamic Covalent Properties and Formation of Stimuli-Responsive Cyclophanes by Self-Assembly. *Angew. Chem., Int. Ed.* **2016**, *55* (30), 8634−8638.

(16) Okino, K.; Hira, S.; Inoue, Y.; Sakamaki, D.; Seki, S. The Divergent Dimerization Behavior of N-Substituted Dicyanomethyl Radicals: Dynamically Stabilized versus Stable Radicals. *Angew. Chem.* **2017**, *129* (52), 16824−16828.

(17) Okino, K.; Sakamaki, D.; Seki, S. Dicyanomethyl Radical-Based Near-Infrared Thermochromic Dyes with High Transparency in the Visible Region. *ACS Mater. Lett.* **2019**, *1*, 25−29.

(18) Peterson, J. P.; Geraskina, M. R.; Zhang, R.; Winter, A. H. Effect of Substituents on the Bond Strength of Air-Stable Dicyanomethyl Radical Thermochromes. *J. Org. Chem.* **2017**, *82* (12), 6497−6501.

(19) Zhang, R.; Peterson, J. P.; Fischer, L. J.; Ellern, A.; Winter, A. H. Effect of Structure on the Spin−Spin Interactions of Tethered Dicyanomethyl Diradicals. *J. Am. Chem. Soc.* **2018**, *140* (43), 14308−14313.

(20) McConnell, H. M. Molecular Orbital Approximation to Electron Coupled Interaction between Nuclear Spins. *J. Chem. Phys.* **1956**, *24* (2), 460−467.

(21) Xie, C.; Lahti, P. M.; George, C. Modulating Spin Delocalization in Phenoxyl Radicals Conjugated with Heterocycles. *Org. Lett.* **2000**, *2* (22), 3417−3420.

(22) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom−atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10* (44), 6615−6620.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. B.01*; Gaussian, Inc.: Wallingford, CT, 2016.

(24) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113* (18), 6378−6396.

(25) Geraskina, M. R.; Dutton, A. S.; Juetten, M. J.; Wood, S. A.; Winter, A. H. The Viologen Cation Radical Pimer: A Case of Dispersion-Driven Bonding. *Angew. Chem., Int. Ed.* **2017**, *56* (32), 9435−9439.

(26) Barone, V. Structure, Magnetic Properties and Reactivities of Open-Shell Species From Density Functional and Self-Consistent Hybrid Methods. In *Recent Advances in Density Functional Methods*; World Scientific Publishing Co. Pte. Ltd.: River Edge, NJ, 1995; pp 287−334.