SUPPORTING INFORMATION

Influence of bridge-reduced state levels on the electron transfer within 2,7-dinitroanthracene radical anion

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Experimental Techniques

2,7-Dinitroanthracene (**3**): 2,7-Dinitroanthracene was prepared by pyrolysis of a mixture of 2,6- and 2,7-dinitro-9,10-ethano-9,10-dihydroanthracene under vacuum[S1] and separated from the 2,6-dinitro isomer by a combination of column chromatography and fractional recrystallization from benzene. mp >300°; *m/z* 268 (M+); ^{1}H NMR (300 MHz; DMSO-*d*6) δ 9.33 (s, H_9), 9.19 (s, $2H_{1,8}$), 8.91 (s, H_{10}), 8.37 (d, $2H_{3,6}$ J=9.3 Hz), 8.26 (d, $2H_{4,5}$ J=9.3 Hz). UV (MeCN): λ_{max}=404 nm (log ε=3.78). EPR (radical anion, MeCN, RT) a_{2N} = 3.00 G, a_{2H} = 4.16 G, a_{2H} = 0.375 G, a_{2H} = 1.00 G, a_H = 3.98 G, a_H = 0.53 G.

Preparation of radical anions

The radical anions were prepared in vacuum-sealed glass cells equipped with an ESR tube and a quartz optical cell. Compound **3**, an excess of commercial cryptand[2.2.2], and 0.3% Na-Hg amalgam were introduced in different chambers of the cell under nitrogen. The cryptand was degassed by melting under high vacuum before addition of the solvent. THF was directly distilled in the vacuum line from an ampoule where it was stored under 1:3 Na/K alloy. MeCN, DMSO and PhCN were dried over CaH_2, decanted and distilled before addition to the cell, and degassed in several pump-thaw cycles. The concentration of the samples was determined spectrophotometrically before reduction. Reduction was achieved by contact with the 0.2% Na-Hg amalgam. UV/vis/NIR spectra were recorded at room temperature at several stages of reduction, so that the maximum radical anion oxidation level spectrum could be selected.

Instrumentation

UV/vis/NIR spectra were obtained with a Shimadzu UV-3101PC spectrometer. EPR spectra were measured in a Bruker esp300e spectrometer. NMR spectra were recorded on a Bruker Avance III 300 spectrometer.

Theoretical Calculations

Structure optimizations and TD-DFT calculations were performed using Gaussian09 at the UB3LYP/6-31+G(2d,p) level and a CPCM solvent model.[S2]

Three-Stage Model

The determinant of equation 1 is an equation of the form

$$a\,E^3 + b\,E^2 + c\,E + d = 0 \qquad \text{S1}$$

with

$$a = 1 \qquad \text{S2}$$

$$b = -(H_a+H_b+H_c) \qquad \text{S3}$$

$$c = H_a.H_b + H_a.H_c + H_b.H_c - H_{ab}^2 - 2\,H_{ic}^2 \qquad \text{S4}$$

and

$$d = -\,H_a.H_b.H_c + H_a.H_{ic}^2 + H_b.H_{ic}^2 + H_c.H_{ab}^2 - 2H_{ab}.H_{ic}^2 \qquad \text{S5}$$

The diabatic surfaces representing the CBUs are given by $H_a = \lambda\, x^2$ and $H_b = \lambda\,(1\text{-}x)^2$, where x is the reaction coordinate, and the diabatic surface representing the bridge is $H_c = \lambda\,(1/2\text{-}x)^2 + \Delta$, where Δ is the vertical energy displacement of the H_c minimum. Although the cubic equation above has three real roots, the formulas expressing these roots often involve imaginary numbers. To avoid this, equation S1 was solved numerically for the whole range of x values using trigonomeric functions.

For delocalized ground states the electronic transitions will be the energy difference of the adiabatic states at x=1/2, and for this point the equation has analytic solutions. For H_{ab}=0 we get

$$X_{1\,(x=0.5)} = \lambda/8 + \Delta/2 - 1/2\,((\Delta-\lambda/4)^2 + 8H_{ic}^2)^{1/2} \qquad \text{S6}$$

$$X_{2\,(x=0.5)} = \lambda/4 \qquad \text{S7}$$

and

$$X_{3\,(x=0.5)} = \lambda/8 + \Delta/2 + 1/2\,((\Delta-\lambda/4)^2 + 8H_{ic}^2)^{1/2} \qquad \text{S8}$$

so the two electronic transitions will be

$$E_{op}^1 = X_2 - X_1 = -1/2(\Delta-\lambda/4) + 1/2\ ((\Delta-\lambda/4)^2 + 8H_{ic}^2)^{1/2} \qquad S9$$

and

$$E_{op}^2 = X_3 - X_1 = ((\Delta-\lambda/4)^2 + 8H_{ic}^2)^{1/2} \qquad S10$$

One should note that the difference

$$E_{op}^1 - 1/2\ E_{op}^2 = -1/2(\Delta-\lambda/4) \qquad S11$$

is independent of the coupling H_{ic} and yields $(\Delta-\lambda/4)$ directly. Once the $(\Delta-\lambda/4)$ value is determined, H_{ic} can be easily extracted from S9 or S10. Using the energies of the two first bands of **3**$^-$ in THF (E_{op}^1 = 4200 cm^{-1} and E_{op}^2 = 12900 cm^{-1}) yields $(\Delta-\lambda/4)$=4500 cm^{-1} and H_{ic}=4275 cm^{-1}. A delocalised ground-state is obtained for $\lambda < 6000$ cm^{-1}, yielding Δ=6000 cm^{-1} for λ = 6000 cm^{-1}. As noted above, equations S6-S11 are only valid for delocalised ground-state surfaces and for H_{ab}=0. Further calculations (for charge-localised ground-states and/or for $H_{ab}\neq0$) were done by solving equation S1 numerically. Changing the solvent to MeCN (where E_{op}^1 = 7670 cm^{-1} and E_{op}^2 = 13000 cm^{-1}) should increase λ significantly, but we couldn't fit the energies of the two bands without decreasing H_{ic}. The best fit was achieved with λ=10200 cm^{-1}, Δ=7000 cm^{-1} and H_{ic}=2800 cm^{-1}.

Optimized Geometry Coordinates

<u>2,7-Dinitroanthracene</u> <u>**3**$^-$</u>, delocalised

```
UB3LYP/6-31+G(2d,p); (cpcm,solvent=thf)
C        0.005581    0.000037   -0.001796
C        0.005775    0.000023    1.417763
C        1.197927    0.000015    2.093996
C        2.448709    0.000018    1.403826
C        2.442330    0.000032   -0.044141
C        1.199915    0.000041   -0.720892
C        3.673210    0.000009    2.084226
C        4.898414    0.000012    1.405076
```

C	4.906251	0.000026	-0.042880
C	3.674642	0.000035	-0.727583
C	6.148482	0.000003	2.096520
C	7.341329	0.000006	1.421504
C	7.342942	0.000019	0.001953
C	6.149360	0.000029	-0.718365
N	-1.236794	0.000046	-0.689506
O	-1.235860	0.000064	-1.942613
O	-2.304635	0.000034	-0.030381
N	8.586052	0.000022	-0.684508
O	8.586416	0.000036	-1.937588
O	9.653178	0.000010	-0.024279
H	-0.939029	0.000020	1.944528
H	1.203757	0.000005	3.179792
H	1.172927	0.000052	-1.802742
H	3.672654	-0.000001	3.171076
H	3.675199	0.000045	-1.814033
H	6.141543	-0.000007	3.182310
H	8.285595	-0.000002	1.949230
H	6.177456	0.000038	-1.800188

2,7-Dinitroanthracene **3**$^-$, localised

UB3LYP/6-31+G(2d,p); (cpcm,solvent=Acetonitrile)

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.426542
C	1.180046	0.000000	2.115263
C	2.442893	-0.000448	1.437750
C	2.443248	-0.000903	-0.012325
C	1.208773	-0.000694	-0.703064
C	3.653797	-0.000407	2.131444
C	4.890398	-0.000773	1.464628
C	4.902338	-0.001211	0.019292
C	3.682066	-0.001285	-0.680896
C	6.131286	-0.000691	2.164789
C	7.331316	-0.001020	1.499112
C	7.326682	-0.001436	0.082011
C	6.151854	-0.001538	-0.648693
N	-1.221273	-0.000056	-0.682514
O	-1.218970	-0.012094	-1.956158
O	-2.315947	-0.010643	-0.027587
N	8.589275	-0.001764	-0.618012
O	8.586354	-0.002961	-1.857416
O	9.636712	-0.002465	0.045887
H	-0.948769	0.000344	1.945724
H	1.174394	0.000389	3.200435
H	1.196306	-0.000891	-1.784464
H	3.641585	-0.000040	3.217449
H	3.697717	-0.001570	-1.766555

H	6.117022	-0.000351	3.249629
H	8.271613	-0.000951	2.031778
H	6.187345	-0.001859	-1.730011

[S1] H. Tanida, H. Ishitobi, *Tetrahedron Lett.*, 1964, **15**, 807.

[S2] Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.