

## Reaction of 1, 1-Di-*p*-methoxyphenyl-2, 2-dinitroethylene and 1, 1-Di-*O*-methoxyphenyl-2, 2-dinitroethylene with 1-Benzyl-1, 4-dihydroni- cotinamide: Evidence for Concerted Electron-hydrogen Atom Transfer Mechanism

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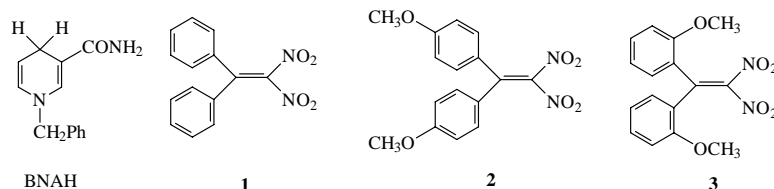
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**Abstract:** 1, 1-Di-*p*-methoxyphenyl-2, 2-dinitroethylene reacts with 1-benzyl-1, 4-dihydronicotinamide (BNAH) in deaerated acetonitrile to give 1, 1-di-*p*-methoxyphenyl-2, 2-dinitroethane, while 1, 1-di-*O*-methoxyphenyl-2, 2-dinitroethylene fails to react with BNAH under the same conditions, which provides evidence for a concerted electron-hydrogen atom transfer mechanism.

**Keywords:** 1, 1-Di-*p*-methoxyphenyl-2, 2-dinitroethylene; 1-di-*O*-methoxyphenyl-2, 2-dinitroethylene; 1-benzyl-1, 4-dihydronicotinamide; curve-crossing model.

NADH is an important coenzyme that plays a vital role in biological redox reactions. The mechanism of reduction of various substrates by coenzyme NADH models has been extensively studied and continues to be of interest<sup>1,2</sup>. Savéant *et al.*<sup>3</sup> have recently reported the investigation on dynamics of proton transfer from the cation radicals of synthetic analogues of NADH with the conclusion that “the proton transfer from the cation radicals is better viewed as a concerted electron-H atom transfer rather than a *stricto sensu* proton transfer”. The Pross-Shaik curve-crossing model<sup>4</sup> proposes that “both SET and polar pathways involve a single electron shift in the transition state region” and “the two mechanisms are distinguished by the degree of concertedness of the electron shift and bond-formation steps”.



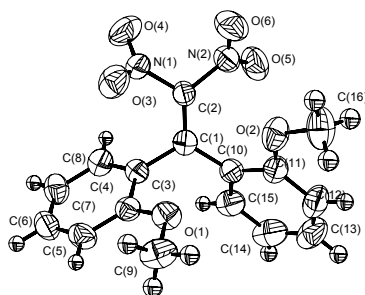
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Recently we<sup>5</sup> reported that the reduction of 1, 1-diphenyl-2, 2-dinitroethylene **1** with 1-benzyl-1, 4-dihydronicotinamide (BNAH) in oxygen-saturated acetonitrile produced 1, 1- diphenyl-2, 2-dinitroethane and benzophenone, which indicated the trapping of a carbon radicaloid species by oxygen in the pathway. A curve-crossing model for the reaction projects that the transition state has partial diradical and partial covalent bonding character. Previously, Bethell *et al.*<sup>6</sup> have reported that in the reaction of 9-arylfluoren-9-yl cations with polymethylbenzenes in trifluoroacetic acid solution “the overall hydride transfer proceeds though a transition state having considerable electron-transfer character and with loosening of the transferred hydrogen.”

In order to test the plausibility of the proposed mechanism for this reaction<sup>5</sup>, we have investigated the reaction of BNAH with 1, 1-di-*p*-methoxyphenyl-2, 2-dinitroethylene **2** and 1, 1-di-*O*-methoxyphenyl-2, 2-dinitroethylene **3**, respectively. If an ortho substitution effect on the rate of reaction<sup>7</sup> should show up, evidence would be provided for a concerted electron transfer-hydrogen atom transfer mechanism of reduction<sup>12</sup>.

The structures of compounds **1** and **2** have been determined by X-ray crystallography<sup>5,8</sup>. The molecular structure<sup>9</sup> of compound **3** is shown in **Figure 1**.

**Figure 1** Molecular structure of **3** showing 50% probability displacement ellipsoids and the atom-numbering scheme

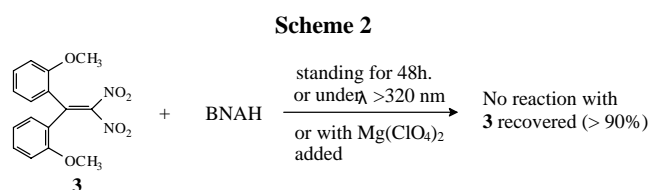
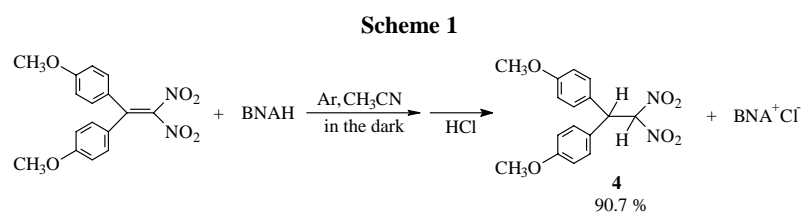


X-Ray analysis showed that these molecules conform closely to idealized  $C_2$  symmetry with the two-fold axis aligned along the C(1)–C(2) double bond. The steric repulsion between the aryl rings and C-NO<sub>2</sub> fragments results in an appreciable twist about the central double bond. By comparison of the dihedral angles listed in **Table 1**, it is seen that compound **3** has the largest angles between aryl rings and between C-NO<sub>2</sub> fragments. This shows clearly that the space around the double bond in **3** is more congested than that in **1** and **2**.

**Table 1** Dihedral angles in compound **1-3**

	<b>1</b>	<b>2</b>	<b>3</b>
Dihedral angle between aryl rings [°]	77.7	62.8	87.4
Dihedral angle between C-NO <sub>2</sub> fragments [°]	68.5	65.9	76.5

When equimolar quantities of **2** and BNAH were dissolved in dry deaerated acetonitrile and the solution was allowed to stand at room temperature for 4.5 h. in the dark, a reaction took place and the products isolated were shown in **Scheme 1**. When equimolar **3** and BNAH were dissolved in dry, deaerated acetonitrile and the solution was allowed to stand under argon for 48 h in the dark, no reaction occurred. When the latter reaction mixture in a Pyrex glass tube was continuously irradiated with a 250 W high-pressure mercury lamp for 48 h, there was still no reaction. Even when an equimolar amount of  $\text{Mg}(\text{ClO}_4)_2$  was added to the mixture, reaction was not detectable (**Scheme 2**). After **3** was reduced with  $\text{NaBH}_4$  in acetonitrile for 2 h, treatment with 0.1 mol/L hydrochloric acid and subsequent work-up gave 1, 1-di-*o*-methoxyphenyl-2, 2- dinitroethane **5** in 90% yield.



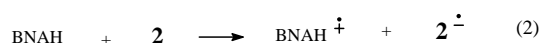
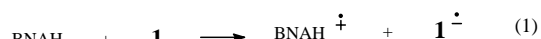
The rates of reactions of **1**, **2** with BNAH in deaerated acetonitrile were measured by HPLC method<sup>10</sup> and second-order rate constants obtained as 0.0141, 0.00751  $\text{M}^{-1} \text{s}^{-1}$ , respectively. The result is rationalized by the electron donating effect of the *p*-methoxy group, which decreases the rate of electron transfer reaction.

The electrode potentials of BNAH and compounds **1-3** were determined by cyclic voltammetry at 50  $\text{mV s}^{-1}$  in acetonitrile, and the results are tabulated in **Table 2**.

**Table 2** Electrode potentials of compounds **1-3** and BNAH in  $\text{CH}_3\text{CN}$  containing 0.1 mol/L  $n\text{-Bu}_4\text{NClO}_4$  at a glassy carbon electrode

Compound	BNAH	<b>1</b>	<b>2</b>	<b>3</b>
E (V vs. Ag/AgCl)	0.63	-0.43	-0.51	-0.61

Consider the following electron transfer reactions:



Since  $E_{\text{ox}}$  for BNAH is higher than  $E_{\text{red}}$  for **1**, **2** and **3**, electron transfer from BNAH to these compounds are all endergonic. However, when electron transfer is coupled with a concerted formation of a C–H covalent bond resulting in a hydride transfer, the intrinsic potential barrier for electron transfer is reduced<sup>4b</sup>, so reaction (1) and (2) can proceed with efficiency as borne out by experiment. On the other hand, in the case of **3**, because the steric effect of the two ortho methoxy groups prevents the approach of BNAH to the  $\beta$ -carbon for hydrogen transfer, the reaction cannot take place. This provides evidence for the notion that hydride transfer from BNAH takes place *via* a concerted electron-hydrogen atom transfer pathway.

### Acknowledgments

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- For compound **1**, see Ref. 5; for compound **2**, see D. M. Dai, Y. C. Liu, H. B. Song, Q. M. Wang and T. C. W. Mak, *J. Chem. Crystallogr.*, in press.
- Crystal data of **3**: C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>, M = 330.29, monoclinic, C2/c,  $a = 12.671(5)$ ,  $b = 15.795(6)$ ,  $c = 16.290(7)$  Å,  $\beta = 108.421(8)^\circ$ ,  $V = 3093(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $\mu = 0.110$  mm<sup>-1</sup>,  $\theta$ -range 2.13-26.09, 3066 independent reflections, refinement on  $F^2$  for 218 parameters,  $wR(F^2, \text{all refl.}) = 0.2142$ ,  $R_1[1224 \text{ obs. refl. with } I > 2\sigma(I)] = 0.0625$ . CCDC deposit No. 209009.
- Owing to the fact that the UV absorption of BNAH and **1**, **2** overlapped to a great extent, the rates of reactions could not be measured by UV spectroscopy.
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- Compounds **2** and **3** were prepared according to the literature method<sup>11</sup>, and cyclic voltammetry was performed by means of a BAS CV-27 Voltammograph using Ag/AgCl electrode as reference with (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup> ClO<sub>4</sub><sup>-</sup> as supporting electrolyte.  
Product **4**: <sup>1</sup>H NMR  $\delta$ (CDCl<sub>3</sub>, ppm), 7.21(d, 4H, J=7.77Hz), 6.88(d, 4H, J=7.77Hz), 6.86(d, 1H, J=11.6Hz), 5.10(d, 1H, J=11.6 Hz), 3.77(s, 6H). HRMS(EI) Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>: 332.1008, Found: 332.0988.  
Product **5**: <sup>1</sup>H NMR  $\delta$ (CDCl<sub>3</sub>, ppm) 7.54(d, 1H, J=19.5Hz), 7.11(m, 8H), 5.75(d, 1H, J=19.5Hz), 3.85(s, 6H); HRMS(ESI) Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>+Na: 355.0901, Found: 355.0906.

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