

Investigation by ^1H and ^{13}C NMR and UV Spectroscopy and by *ab-initio* Calculations of a Novel Enedione Anion-Radical Dimerization

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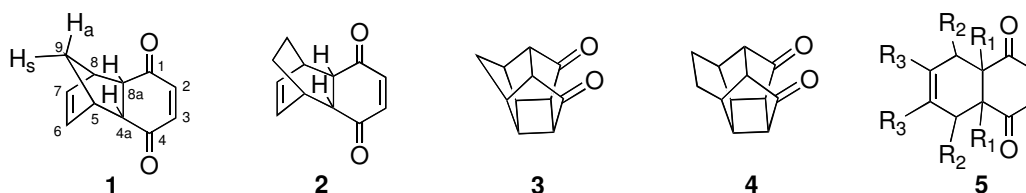
Abstract: After 6 h in the dark, in the absence of oxygen, an ethanol / triethylamine solution of 4a,8a-cis-endo-5,8-methano-4a,5,8,8a-tetrahydronaphthalen-1,4-dione gives rise to a novel dimer of this enedione, which is unattainable by photochemistry. The elucidation of the structure of this dimer, by the combined application of ^1H and ^{13}C NMR and UV spectroscopy and by *ab-initio* GIAO//B3PW91/6-31G* calculations, is described and a mechanism of formation is proposed.

Introduction

In 1964, Cookson *et al.*¹ demonstrated that 4a,8a-cis-endo-5,8-methano-4a,5,8,8a-tetrahydronaphthalen-1,4-dione (**1**) and its 5,8-ethano homologue (**2**) — which are, respectively, the adducts of benzoquinone and cyclopentadiene or cyclohexadiene — photocyclize to their corresponding *intra*-molecular [2+2] cycloadducts (**3** and **4**, respectively) upon exposition to UV light, both in solution or as pure crystals. Later, Scheffer and coworkers^{2,3} have shown that UV irradiation of

benzoquinone/diene adducts lacking a methano or ethano bridge (**5**) leads to molecular rearrangement, when in solution, and that, as pure crystals, many of them afford the corresponding dimers (*i. e.* *inter*molecular [2+2] cycloadducts). Being unreachable by photochemical means, the dimers of compounds **1** and **2** have never before been described in the literature.

Now we report a simple thermal reaction, unveiled in the course of our on-going investigations^{4,5} on enediones, that yields unequivocally a dimer (**6**) of compound **1**.



Experimental Section

Compound **1**⁶ and anhydrous ethanol⁷ were prepared according to literature procedures, while triethylamine (TEA) was distilled from sodium wire before use.

A Varian Unity Inova 300 spectrometer was employed for measuring the ^1H and ^{13}C NMR spectra (in CDCl_3 solutions, TMS=0) at 300 and

75 MHz, respectively, using instrumental settings akin to those described previously.⁸⁻¹⁰ *J* values are given in Hz. All assignments were established by combining information from NOEDIF, DEPT and HETCOR experiments.

Elemental analysis was carried out on a Perkin-Elmer 2400-CHN instrument. The electrospray ionization mass spectrum (ESI/MS)

was obtained in a Micromass Quattro II mass spectrometer and the UV-visible spectra were measured with a Hitachi U-2000 spectrophotometer.

Solvent removal was effected in a Buchler PTFE-1GN flash-evaporator, using a PF-1029 Continuous Feed Adapter (**CFA**), modified by sealing to its hose-barb end (at an angle of 90°) the wider end of a Pasteur pipette. Reduced pressure was achieved with a Chapman-type swirling high-throughput aspirator-pump driven by water (kept at 25 °C) from a 2 hp circulating pump.

The *ab-initio* calculations were performed using the GAUSSIAN 98, Revision A.9, package of molecular orbital programs.¹¹ Initial geometries of compounds **6a-d** were attained by the semi-empirical PM3 method, and then optimized by RHF, then by DFT calculations at B3PW91 level of theory, using the 6-31G* basis set. Chemical shift values were obtained relative to the isotropic shielding tensors of TMS, which were calculated by the same method, at the same level of theory and with the same basis set used for geometry refinement.

endo-cisoid-cis-transoid-cis-cisoid-endo-Tricyclo[16.2.1.1^{8,11}.0^{2,17}.0^{4,15}.0^{5,14}.0^{7,12}]docosa-9,19-dien-3,6,13,16-tetraone (6a).— A solution of 1.0 g (5.7 mmol) of the *cis-endo* enedione **1** in 100 cm³ of anhydrous ethanol was deaerated by a slow current of (anhydrous, oxygen-free) ethanol-saturated argon, under sonication, for 20 min. Meanwhile, in a separate vessel, 20 cm³ of anhydrous **TEA** was likewise deaerated with **TEA**-saturated argon. The **TEA** was then added in the dark to the ethanolic solution of **1**, the system was left undisturbed and protected from light for 6h and the solvent was removed under reduced pressure. Then 100 cm³ of aqueous-methanolic 15% hydrochloric acid solution was aspirated in through the modified **CFA**, being afterwards evaporated, still under reduced

pressure, and this procedure was twice repeated. Finally 100 cm³ of chloroform was aspirated in, the flask rotated to dissolve all solid materials and air admitted in. The organic layer was separated and the aqueous phase was washed thrice with 20 cm³ portions of chloroform. These washings were reunited to the organic layer, which was then dried with anhydrous magnesium sulfate, and filtered. After evaporating the chloroform, the resulting residue was purified by preparative TLC on silica-gel with hexanes/ethyl acetate (9:1), affording 0.5 g of **6a** as a colorless oily grease, which failed to crystallize. Yield: 50% (isolated). Found: 75.7 %C; 5.6 %H (C₂₂H₂₀O₄ requires 75.84 %C and 5.79 %H); δ (¹H): 1.27 (bd, J = 9.90, H21a,22a); 1.48 (dt, J = 9.90, 1.65, H21s,22s); 3.31 (m, H1,8,11,18); 3.45 (dd, J = 2.10, 1.20, H2,7,12,17); 3.52 (s, H4,5,14,15); 6.05 (t, J = 1.80, H9,10,19,20); δ (¹³C): 43.38 (C1,8,11,18); 46.40 (C21,22); 49.52 (C2,7,12,17); 57.86 (C4,5,14,15); 136.71 (C9,10,19,20); 204.02 (C3,6,13,16); m/z (rel. int.) 348.40 (100%); 349.40 (24.73%) 350.40 (4.01%); (C₂₂H₂₀O₄ requires M⁺: 100%; M⁺+1: 25.10%; M⁺+2: 3.83%).

Results and Discussion

We have found out that, surprisingly, **6** is obtained as the main product six hours after the addition of 17% (v/v) triethylamine (**TEA**) to an ethanolic solution of **1**, in the absence of light, under deaerated conditions. On comparing the UV absorption spectrum of **1** in ethanol and in a freshly prepared deaerated solution in 17% (v/v) ethanol / **TEA** (Figure 1) we found out that they are noticeably different and that a new band is observed at 294 nm, when **TEA** is present, indicating that a new species (**X**) must be present. This new species must arise from a reversible reaction, since removal of the **TEA** just a few minutes after its addition results in

almost quantitative recovery of **1**, while letting **TEA** remain in the reaction medium for longer

periods lead to the formation of **6**, a fact which shows that the dimerization is a slow reaction.

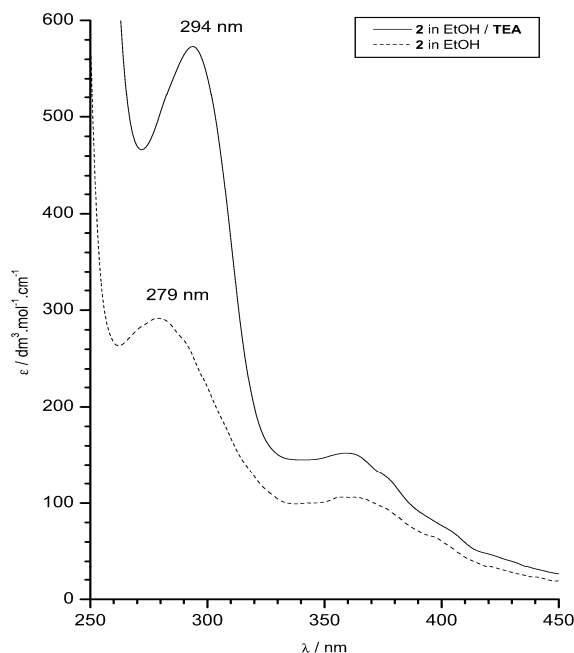
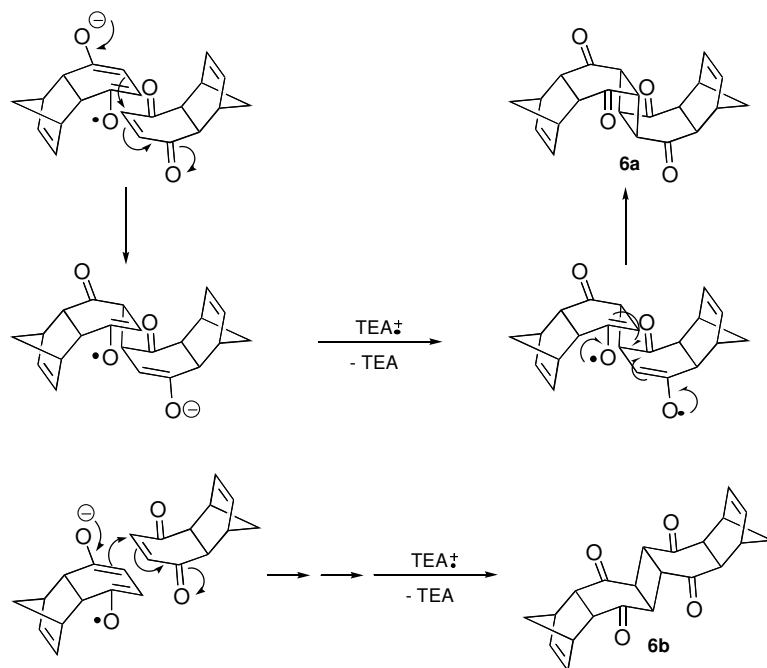


Figure 1. UV-visible absorption spectra of compound **1**, at 298K, in the indicated solvents.

Pandey *et al.*¹²⁻¹⁴ have reported many results due to the photochemistry of enedione anion-radicals, obtained by adding **TEA** to deaerated solutions of enediones in ethanol, followed by exposition of the resulting solutions to UV light. They interpreted their results assuming the occurrence of Photoinduced Electron Transfer (PET) from **TEA** to an excited state of the enediones. If it were so, there ought not to be any new species present in the system prior to irradiation. So, in view of our results, we concluded that single electron transfer occurs from **TEA** to the enedione *in the ground state*, and hence, that **X** must be the anion-radical

derived from **1** via intermolecular charge transfer with **TEA**, and envisaged the formation of **6** as being due to the reaction between enedione **1** and its radical anion, as depicted in Scheme 1 (for **6a** and **6b**; the formation of **6c** and **6d** can be written analogously). The new dimer **6** is the result of joining two molecules of **1** by cycloaddition of their enedione double-bonds, leading to a cyclobutane, as is attested by the diagnostic presence of a singlet at 3.52 ppm (and the absence of any signal attributable to hydrogens attached to an enedionic double-bond) in the ¹H NMR spectrum of purified **6** (Figure 2).



Scheme 1. The Enedione Anion-radical Dimerization.

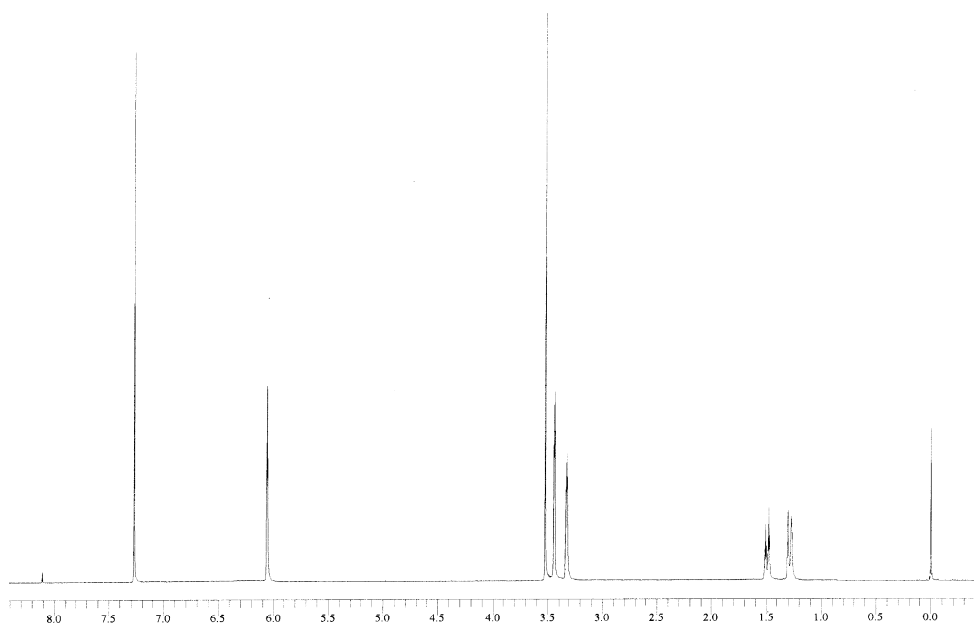


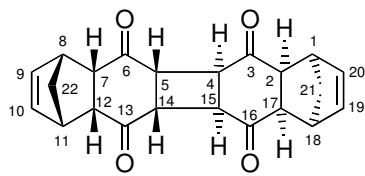
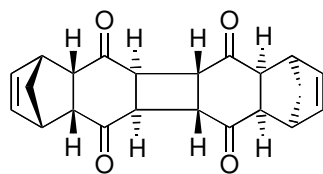
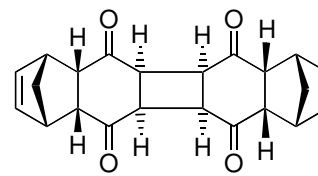
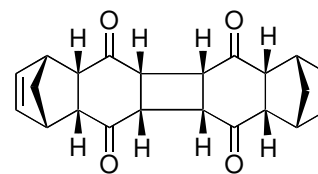
Figure 2. ^1H NMR spectrum of compound **6**, at 298K, in deuteriochloroform with TMS.

This newly-formed cyclobutane (**6**) must be either one of the *transoid*-isomers (**6a** or **6b**) or

the *cisoid*-isomer **6c**, since the formation of the other *cisoid*-isomer (**6d**) is not possible because

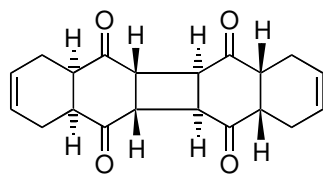
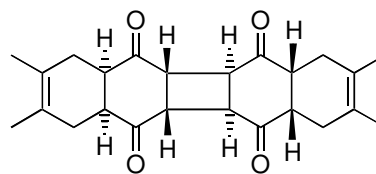
it would require the reactants to meet in a stacked arrangement, which is prevented by mutual steric hindrance. In fact, Dekker *et al.*¹⁵ have found out that, in the photochemical dimerization (in solution) of the less bulky 1,4-naphthoquinone, the total product consists mainly of the *transoid* dimer, containing only

0.25% of its *cisoid*-isomer. Molecular models show that formation of isomer **6c** has somewhat less steric hindrance than the *cisoid*-dimer of naphthoquinone, while, for **6d**, there is even more hindrance, so that it surely cannot be formed in solution.

**6a****6b****6c****6d**

The ¹H NMR spectrum of compound **6** contains just one singlet at 3.52 ppm (from the four protons in the cyclobutane ring), while its ¹³C NMR spectrum shows one single carbonyl signal at 204.02 ppm. This implies that **6** presents one bilateral symmetry plane containing both methano-bridge atoms and one C₂ axis, and must have either C_{2h} (**6a** or **6b**) or C_{2v} (**6c** or **6d**) symmetry.

Scheffer and Dzakpasu² have prepared the only previously reported dimers akin to isomer **6b** (compounds **27b** and **27c** in ref. 2, here numbered **7a** and **7b**, respectively). They observed that the cyclobutane-ring protons of their compounds give rise to a singlet at 3.64 ppm in the ¹H NMR spectrum, while ours has the singlet at 3.52 ppm, hence it is not the **6b** diastereomer.

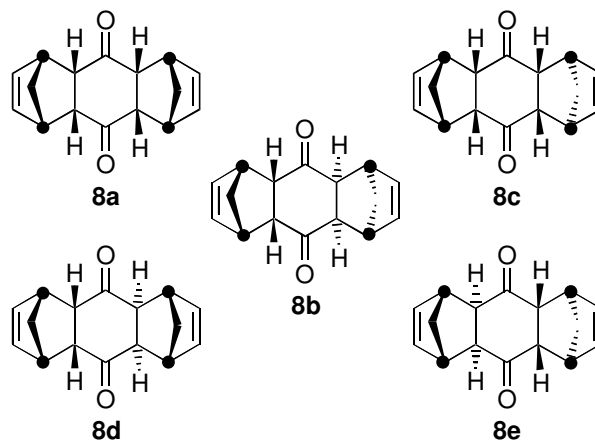
**7a****7b**

The ¹³C NMR data presented by Yates and Switlak¹⁶ for the various diastereomers of the bisadducts of cyclopentadiene and benzoquinone (compounds **12-16** in ref. 9, here numbered **8a-e**, respectively) present the signals corresponding to the norbornenic

methano bridge-head carbons (represented as black dots in the formulae below) either at ca. 44 (**8a** and **8c**) or at ca. 48 ppm (**8b**, **8d** and **8e**), depending on the isomer considered. With the help of molecular models, we found out that those isomers in which the dihedral angle

defined by the carbonyl and its α and β carbons (the nearest bridge-head carbon being the β carbon) can attain any value between 0 and 180° during rotameric motion give rise to the *ca.* 48 ppm signal. The isomers where ring-strain limits that dihedral angle to values between 0

and 90° during rotameric motion show that signal at *ca.* 44 ppm (due to the γ -gauche effect exerted by the carbonyl oxygen onto the bridge-head carbon, which operates only in *synclinal* or *synperiplanar* rotamers).



Molecular models show that isomers **6b** and **6c** have the same type of 180° dihedral angle rotameric freedom as the related bisadducts of cyclopentadiene and benzoquinone, while more strained **6a** can only attain an angle of not more than 90° between the carbonyl and its α and β carbons, during rotameric motion. Hence, the signal at 43.38 ppm in the ^{13}C NMR, due to carbons 1, 8, 11 and 18 of our dimer, confirms it is the **6a** isomer.

Of course, it was necessary to firmly exclude any possibility of *endo-exo* isomerization at C-2,7,12,17 (because, if present, such an isomerization would complicate further the detailed structural elucidation of compound **6**), and hence $\{^1\text{H}\} - ^1\text{H}$ NMR NOEDIF experiments⁸ were performed and they confirmed that the *endo* configuration of **1** is retained in **6a**, as expected: a 3% nuclear Overhauser effect enhancement of the signal at

1.27 ppm (H-21a and H-22a in **6a**)^{8,17,18} is observed upon irradiation at 3.45 ppm (H-2,7,12,17), thus establishing that both 2,17 and 7,12 ring-junctions are *endo* (therefore, these four protons are *exo* and near to either H-21a or H-22a, as suitable).

For the sake of completeness, we have performed *ab-initio* GIAO//B3PW91/6-31G* calculations for all four structures, **6a-d**. The results from these calculations unambiguously exclude structures **6c** and **6d** from consideration, because they demonstrate that such compounds would present, in the ground-state, Cs and C2 symmetry, respectively, and hence lack enough symmetry to be consistent with the observed ^1H and ^{13}C NMR spectra. The ^1H and ^{13}C NMR chemical-shifts, both experimental and calculated for **6a** and **6b** are presented in Table 1.

Table 1. Chemical Shifts from Compound **6**

	GIAO//B3PW91/6-31G* calculated values		Experimental values
	6a	6b	6a
H-01/08/11/18	3,013	3,262	3,319
H-02/07/12/17	3,584	3,736	3,434
H-09/10/19/20	6,315	6,271	6,053
H-04/05/14/15	3,518	2,992	3,520
H-21s/22s	1,449	1,491	1,480
H-21a/22a	1,054	1,115	1,270
C-01/08/11/18	45,182	46,364	43,381
C-02/07/12/17	57,042	51,808	57,862
C-03/06/13/16	201,918	198,919	204,017
C-04/05/14/15	47,668	45,899	49,518
C-09/10/19/20	132,403	133,616	136,712
C-21/22	47,282	46,954	46,400

Linear regression analyses of both calculated datasets presented in Table 1 *versus* the experimental data show acceptable correlation in both cases, but both the correlation coefficients (r) and, most notably, the standard-

errors (σ) of the estimates, listed in Table 2, clearly point to structure **6a** as the best solution, as also do the Relative Total Ground-State Energies (also in Table 2), resulting from the *ab-initio* calculations.

Table 2. Results for Compound **6**

Isomer	Relative Energy ^a	r (¹ H)	σ (¹ H)	r (¹³ C)	σ (¹³ C)
6a	0,00	0,9966	0,174	0,9997	1,901
6b	6,19	0,9886	0,310	0,9989	3,402

^a in kcal.mol⁻¹

Conclusion

In short: herein, a novel reaction, leading to a previously unknown dimer of 4a,8a-*cis-endo*-5,8-methano-4a,5,8,8a-tetrahydronaphthalen-1,4-dione is described, and a detailed elucidation of both structure and stereochemistry of this new compound is provided.

Acknowledgments

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