

Revised Structure of a Purported 1,2-Dioxin: A Combined Experimental and Theoretical Study

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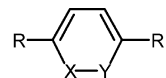
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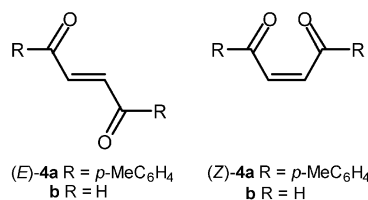
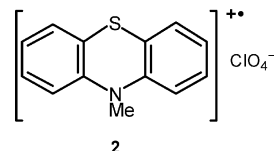
Abstract: 3,6-Bis(*p*-tolyl)-1,2-dioxin (**1g**) was suggested by Shine and Zhao as a product in an electron-transfer (ET) photochemical reaction. This photoproduct is instead shown to be (*E*)-1,4-di-*p*-tolylbut-2-ene-1,4-dione ((*E*)-**4a**). Ab initio and DFT calculations indicate that ring-closed 1,2-dioxin is thermodynamically far less stable than open-chain but-2-ene-1,3-dione. These calculations indicate that (*E*)-**4a** is formed via the cation radical of **1g**, which sequentially isomerizes to a novel σ -radical with an O,O 3e bond [(*Z*)-**4a**]⁺⁺, undergoes ET to give (*Z*)-**4a**, and then photoisomerizes to (*E*)-**4a**.

Since the isolation of thiarubrines (e.g., **1a,b**; found in plants of the sunflower family), which incorporate the novel 1,2-dithiin heterocyclic ring system, 1,2-dithiins have attracted considerable attention on several accounts.¹ The challenge of the synthesis of the naturally occurring thiarubrines, the parent heterocycle **1c**, and a number of its derivatives has been met by us and others. We have also prepared 1,2-diselenin (**1d**) and 2-selenathiin (**1e**).^{1,2} We have determined the structures of **1c–e** by microwave spectroscopy,³ elucidated the photochemistry of simple 1,2-dithiins as well as the thiarubrines, examined the electrochemical and chemical oxidation of **1c–e** and some of their derivatives, and measured and interpreted the photoelectron spectra of these compounds.¹ Consequently, we were interested in the oxygen analogue of these compounds, 1,2-dioxin (**1f**). A stable derivative of **1f**, namely, **1g**, was reported in the litera-

ture.^{4,5} This paper reports our reassignment of the structure of **1g** and theoretical studies on its formation.

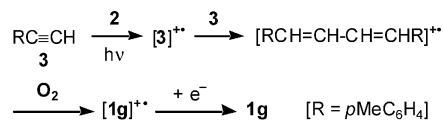


- 1a** X = Y = S, R = CH₂=CHC≡CC=C, R' = MeC≡C-
1b X = Y = S, R = CH₂=CHC≡C, R' = MeC≡CC=C-
1c X = Y = S, R = R' = H
1d X = Y = Se, R = R' = H
1e X = S, Y = Se, R = R' = H
1f X = Y = O, R = R' = H
1g X = Y = O, R = R' = *p*-MeC₆H₄-



Shine and Zhao reported the formation of 1,2-dioxin **1g** on irradiation of 10-methylphenothiazine cation radical perchlorate **2** and *p*-tolylethyne **3** with visible light ($\lambda > 400$ nm).⁴ Scheme 1 shows the mechanism suggested

SCHEME 1



for formation of **1g**.⁴ However, the IR, ¹H NMR, and mass spectra reported for **1g** are identical with those obtained by us for the known (*E*)-1,4-di-*p*-tolylbut-2-ene-1,3-dione ((*E*)-**4a**).⁶ Therefore, we suggest that (*E*)-**4a**, not **1g**, is formed in the reaction studied by Shine and Zhao.⁴ To better understand this system and the mechanism for forming (*E*)-**4a**, DFT calculations were performed.⁷

1,2-Dioxin (**1f**) and (*Z*)-but-2-ene-1,3-dione ((*Z*)-**4b**) are valence isomers. Cis–trans photoisomerization of (*Z*)-**4b** would afford (*E*)-**4b**, which is the parent of the photo-

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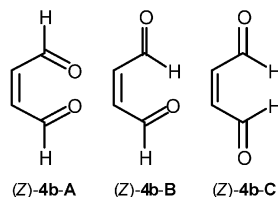
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TABLE 1. Calculated Relative Energies (ΔE) and Relative Enthalpies (ΔH) for Conformers of (*Z*)-4b and Dioxin 1f

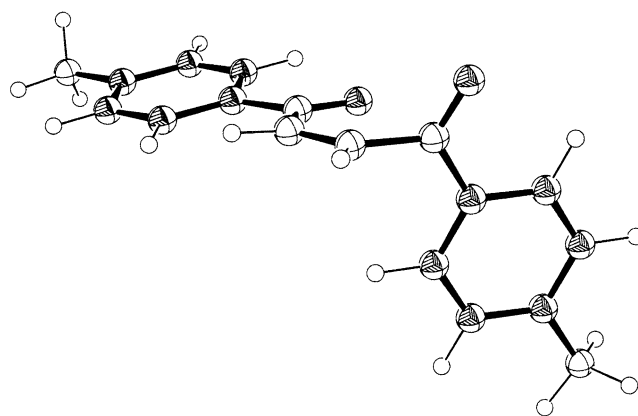
structure	ΔE (ΔH), kcal/mol	
	G2(MP2) ^a	DFT ^b
1f	0.0 (0.0)	0.0 (0.0)
(<i>Z</i>)-4b-A	c	c
(<i>Z</i>)-4b-B	-65.9 (-65.0)	-66.1
(<i>Z</i>)-4b-C	-66.8 (-65.9)	-67.2

^a See ref 8b for the ab initio method used. Energies shown include the change in zero-point energies. ^b DFT calculations using B3LYP/6-31+G*. ^c This conformation is not a local energy minimum.

product (*E*)-4a that we suggest was obtained by Shine and Zhao.⁴ There are three planar conformers of (*Z*)-4b, namely, (*Z*)-4b-A, (*Z*)-4b-B and (*Z*)-4b-C. Their relative energies, including zero point energies, were calculated by G2(MP2)⁸ and compared with that of 1,2-dioxin (**1f**). The results are shown in Table 1.



Conformer (*Z*)-4b-A is not a local energy minimum, presumably due to steric and repulsive electronic interactions, so its energy was not calculated. These calculations were also done using density functional theory (DFT),⁹ and the results are shown in Table 1 as well. As seen in Table 1, the relative energies (ΔE) for these calculations using the B3-LYP functional¹⁰ and the 6-31+G* basis set differ by less than 1 kcal/mol from those of the G2(MP2) calculations. Since DFT methods are computationally less demanding than high-level ab initio calculations but the results are comparable, B3-LYP/6-31+G* calculations were done on the substituted compounds **1g** and (*Z*)-4a. These calculations show that (*Z*)-4a is more stable than **1g** by 63.2 kcal/mol.¹¹ Thus, the purported product **1g** obtained by Shine and Zhao⁴ is much less stable than its valence tautomer (*Z*)-4a. The computationally obtained optimized structure for (*Z*)-4a is depicted in Figure 1. The central fragment of this enedione is twisted about its single bonds. The plane of the ring of one of the tolyl residues is nearly perpendicular to the remaining main molecular fragment that is almost planar. The compu-

**FIGURE 1.** Calculated structure of (*Z*)-1,4-di-*p*-tolylbut-2-ene-1,4-dione ((*Z*)-4a).**TABLE 2. Calculated^a Geometries and Relative Energies (ΔE) for Cation Radicals [**1f**]⁺, [(*Z*)-4b-A]⁺, and [(*Z*)-4b-B]⁺**

structure	symmetry	ΔE , kcal/mol
[1f] ⁺	planar, C_{2v}	0.0
[(<i>Z</i>)-4b-A] ⁺	planar, C_{2v}	-29.1
[(<i>Z</i>)-4b-B] ⁺	planar, C_s	-25.8

tationally obtained optimized structure of **1g** shows that the 1,2-dioxin ring adopts the half-chair conformation, which is characteristically found in other 1,2-dichalcogenins.³ The COOC torsion angle is 60.6°, and the tolyl rings are tilted by 20.5° with respect to the plane of the butadiene fragment of the 1,2-dioxin ring.

Since the proposed mechanism for the reaction, shown in Scheme 1, postulates the formation of the cation radical of **1g**, DFT calculations were performed on a model for this species, [**1f**]⁺. Since ring-opened (*E*)-4a is formed in this reaction, computations on a model for [(*Z*)-4a]⁺, i.e., [(*Z*)-4b-A]⁺, as well as [(*Z*)-4b-B]⁺, were also carried out. These calculations were carried out using the spin-unrestricted DFT method.¹² The results are summarized in Table 2. The lowest energy structure of [**1f**]⁺ is planar, in contrast to its twisted parent **1f**. This is analogous to the results obtained with 1,2-dithiins in which the parent is twisted but the cation radical is planar. In addition, [**1f**]⁺ is less stable than [(*Z*)-4b-A]⁺, as seen in Table 2. Furthermore, a transition structure between [**1f**]⁺ and [(*Z*)-4b-A]⁺ with a single imaginary frequency was found. This leads to a calculated barrier between these two cation radicals of 1.2 kcal/mol.¹³ Thus, [**1f**]⁺ is expected to rapidly isomerize to the more stable [(*Z*)-4b-A]⁺ due to this very low barrier. Furthermore, as seen in Table 2, [(*Z*)-4b-A]⁺ is more stable than [(*Z*)-4b-B]⁺, although (*Z*)-4b-B is more stable than (*Z*)-4b-A. To address these issues, the frontier molecular orbitals in the cation radicals were analyzed. The interaction between the lone pairs of the adjacent oxygen atoms results in a doubly and a singly occupied orbital (SOMO)

(8) (a) Curtiss L. A.; Ragahavachari, K. In *Encyclopedia of Computational Chemistry*; Schleyer P. v. R., Ed.; Wiley: Chichester, UK, 1998; Vol. 2, p 1104–1114. (b) G2(MP2) is a composite technique of ab initio quantum chemical calculations used to obtain accurate energies of molecular systems. Optimum geometry and energy were calculated by MP2/6-31G(d) and two single-point calculations, MP2/6-311+G(3df, 2p) and QCISD(T)/6-311G(d, p).

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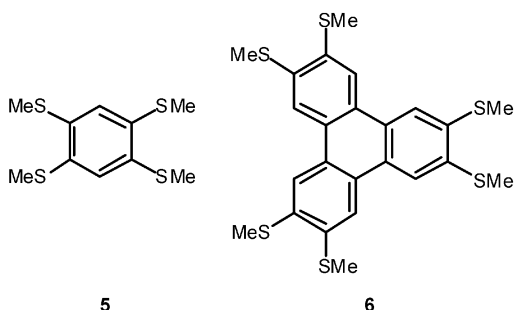
(11) For ring opening of **1f**, $\Delta\Delta H_f$ by MINDO/3 is 51.5 kcal/mol; Pichko, V. A.; Simkin, B. Ya.; Minkin, V. I. *J. Org. Chem.* **1992**, *57*, 7087–7092.

(12) Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1–97 and references therein.

(13) This contrasts with the 13.7 kcal/mol barrier for ring opening of 1,2-dioxin calculated¹¹ by MINDO/3. A significant barrier for ring opening of **1f** supports the observation of a significant lifetime for 1,4-diphenyl-2,3-benzodioxin despite a ca. 90 kcal/mol exothermic ring opening.⁵

in [(*Z*)-**4b-A**]⁺, resulting in a net stabilization. There is a stabilizing pericyclic “partial” O–O bond that is similar to the 2c,3e bond in cation radical water dimers.¹⁴ Thus, [(*Z*)-**4b-A**]⁺ is a σ -type radical in contrast to the π -type radical [**1f**]⁺. The relationship between [**1f**]⁺ and [(*Z*)-**4b-A**]⁺ is analogous to that in *o*-dialkylthioarene cation radicals in which a π -radical or a σ -radical 2c,3e bond between the sulfur atoms can be formed. For example, **5** preferentially forms a π -radical, but **6** forms a σ -radical.¹⁵

The attractive interaction between the oxygen atoms in [(*Z*)-**4b-A**]⁺ is absent in (*Z*)-**4b-A**, where both MOs are doubly occupied, and in [(*Z*)-**4b-B**]⁺, where the oxygen atoms are geometrically precluded from such interaction. Careful comparison of the bonding in [(*Z*)-**4b-A**]⁺ and (H₂O)₂⁺ reveals that the O,O 3e bond is localized in (H₂O)₂⁺ but delocalized in [(*Z*)-**4b-A**]⁺. To better model [(*Z*)-**4b-A**]⁺, calculations were performed on the hypothetical formaldehyde cation radical dimer (HCHO)₂⁺. Visualization of the frontier orbitals by the program MOLDEn¹⁶ shown in Figure 2 reveals that intermolecular interactions in [(*Z*)-**4b-A**]⁺ are very similar to and more delocalized than those in (HCHO)₂⁺. The energetic stabilization in [(*Z*)-**4b-A**]⁺ is also reflected in the calculated O–O bond length and the Wiberg indices¹⁷ calculated by the NBO program.¹⁸ The relatively short O–O bond length of 2.15 Å is comparable to that of (HCHO)₂⁺, which is 2.11 Å. The O–O Wiberg bond indices for [(*Z*)-**4b-A**]⁺ and (HCHO)₂⁺ are 0.25 and 0.19, respectively, confirming the characteristic partial bond between these nominally “nonbonded” atoms. The calculations also show that the energies for the uptake of an electron by [**1f**]⁺ and [(*Z*)-**4b-A**]⁺ in a vertical process is strongly favored by 3.4 eV.



In summary, the product **1g** obtained by Shine and Zhao⁴ is reassigned structure (*E*)-**4a**. Theoretical calculations suggest that this product is formed as previously suggested⁴ but that [**1g**]⁺ isomerizes to [(*Z*)-**4a**]⁺, a novel σ -radical with an O,O 3e bond. Electron transfer to [(*Z*)-**4a**]⁺ generates (*Z*)-**4a**, which photoisomerizes to (*E*)-**4a**.¹⁹ It is also possible that [(*Z*)-**4a**]⁺ first photoisomerizes to [(*E*)-**4a**]⁺ and the latter undergoes electron transfer to (*E*)-**4a**.

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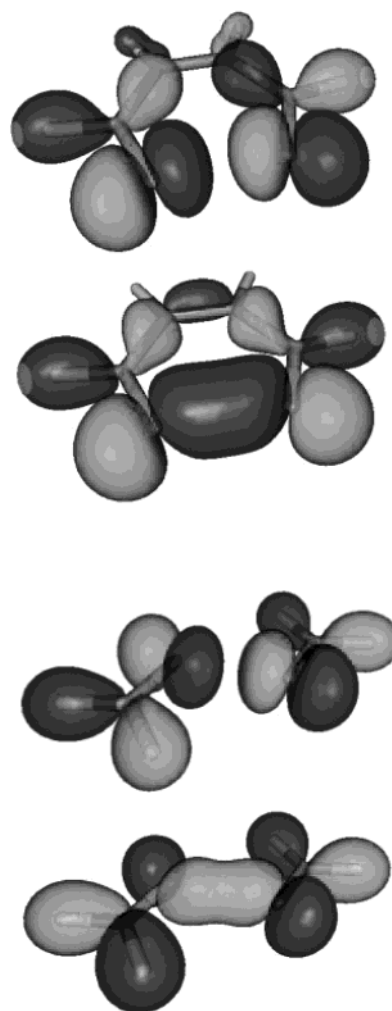


FIGURE 2. Pictorial presentation of the MOs involved in the 3c,2e bond of cation radical [(*Z*)-**4b-A**]⁺ (top two) and the formaldehyde radical cation dimer (bottom two) by MOLDEn. Two electrons occupy the symmetrical MOs, and one electron occupies the antisymmetrical MO in each case.

Experimental Section

(*E*)- and (*Z*)-1,4-Di-*p*-tolylbut-2-ene-1,4-dione [(*E*)- and (*Z*)-4a**].** Following the procedure of Conant and Lutz^{6a} on a one-tenth scale, (*E*)-**4a** was isolated as a colorless solid: mp 143–144 °C; ¹H NMR δ 7.98 (s, 2H), 7.96 (d, *J* = 8.2 Hz, 4H), 7.31 (d, *J* = 8.1 Hz, 4H), 2.43 (s, 6H); ¹³C NMR δ 189.5 (C=O), 145.0, 135.0, 134.5, 129.6, 129.1, 21.8; IR (neat) 1649, 1608, 1326, 1302, 744 cm⁻¹ (among other bands); EI-GC-MS 264 (22%, M⁺), 145 (4%), 119 (100%), 91 (69%), 65 (44%). The IR, MS, and ¹H NMR data for (*E*)-**4** is virtually identical to that reported by Shine⁴

(19) Calculations were performed with the GAUSSIAN 98 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Daniels, A. D.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

for **1g** (^{13}C NMR data was not reported by Shine; our ^1H and ^{13}C NMR data agree with that previously reported for (*E*)-**4a**^{6b}). Overnight exposure of (*E*)-**4a** to light afforded (*Z*)-**4a**: mp 119–121 °C; ^1H NMR δ 7.82 (d, $J = 8.2$ Hz, 4H), 7.21 (d, $J = 8.0$ Hz, 4H), 7.08 (s, 2H), 2.37 (s, 6H); ^{13}C NMR δ 192.0 (C=O), 144.3, 135.3, 133.7, 129.4, 128.7, 21.7; MS identical to that of (*E*)-**4a**; ^1H and ^{13}C NMR data agree with that previously reported for (*Z*)-**4a**.^{6b}

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92-375008086), the Petroleum Research Fund, administered by the American Chemical Society (E.B), the “Fonds der Chemischen Industrie”, and the “Deutsche Forschungsgemeinschaft” (J.F.).

Supporting Information Available: Tables giving the Cartesian coordinates of 1,2-dioxin, 1,2-dioxinium, and open-chain valence isomers optimized by MP2/6-31G* (including G2-(MP2) energies) and DFT (B3-LYP/6-31G*). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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