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# Experimental and computational studies of naphtho[2,3-*c*]tropone: a highly polarized novel troponid system

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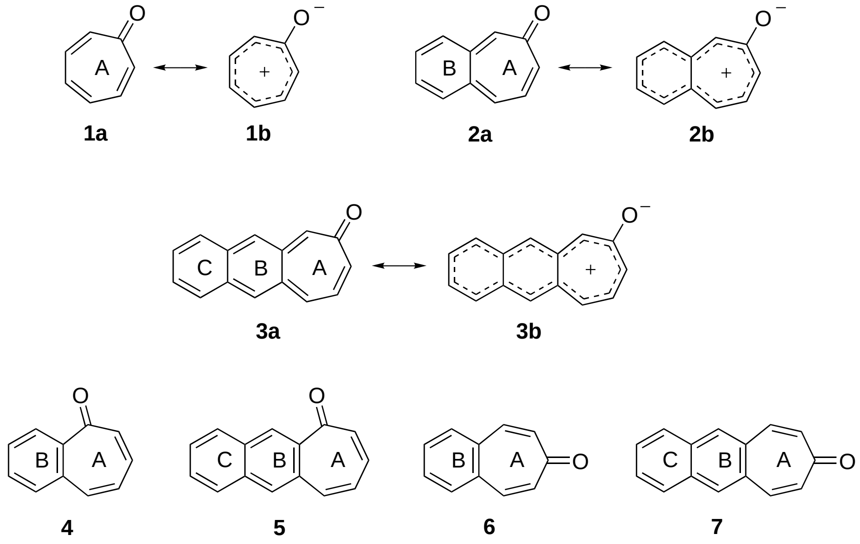
**Abstract**—Irradiation of 6,7-(2′,3′-naphtho)bicyclo[3.2.0]hepta-3,6-dien-2-one (**10**) in a rigid glass at −196°C leads to the formation of hitherto unknown naphtho[2,3-*c*]tropone (**3**), which exhibits a characteristic UV–vis absorption extending to 700 nm and undergoes rapid [π12+π14] dimerization upon thawing the glass. NICS(1) values calculated for a series of benzo- and naphtho-fused tropones suggest that aromatic character of the tropone ring in **3** is significantly increased relative to the parent system. © 2001 Elsevier Science Ltd. All rights reserved.

Tropone (**1**) possesses some aromaticity owing to the contribution of electronically polarized resonance form **1b**.[1] As reported previously,[2] the annelation of benzo group at the 3,4-position of tropone to generate *o*-quinoidal **2** leads to the increased polarization of the C=O bond, suggesting the enhancement of aromaticity at least in the tropone moiety. Here we report the first preparation of naphtho[2,3-*c*]tropone (**3**) as a labile species prone to dimerize and the theoretical evaluation of aromaticity of **2**, **3**, and related compounds. According to the theoretical calculations, the degree of electronic polarization is further enhanced in **3** as compared to that in **2** and the aromaticity of the tropone ring of **3** is significantly increased at the expense of the fused benzenoid rings to exceed that of not only **1** but also **2**, whereas the fusion of benzene or naphthalene ring to the 2,3- or 4,5-position of tropone leads to the diminution of aromaticity in the resulting tropone moiety (Scheme 1).[3,4]



**Scheme 1.**

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On the basis of our previous successful generation of **2** from the corresponding benzocyclobutene valence isomer,[2] we envisaged **10** as a promising precursor for **3** and compound **10** was prepared as illustrated in Scheme 2. Photocycloaddition of 2-cyclopentenone with (*E*)-1,4-dichloro-2-butene followed by protection of the carbonyl group and subsequent two-fold dehydrochlorination produced diene **8**. The Diels–Alder reaction of **8** with benzyne followed by dehydrogenation with DDQ gave **9**, from which **10**[5] was obtained via a sequence of reactions indicated.

When a degassed EPA (a 5:5:2 mixture of ether, isopentane and ethanol) solution of **10** in a Pyrex tube was irradiated with a high-pressure mercury lamp at liquid nitrogen temperature (−196°C), development of an intense absorption was observed in the range of 520–700 nm (Fig. 1). The generated blue–green species was stable in the frozen EPA glass but was consumed rapidly even below −100°C when the glass was thawed. HPLC analysis of the resultant photolysate indicated clean formation of two products (ca. 1:1), which were isolated and unambiguously characterized as *syn*-[π12+π14] dimers **11** and **12** by X-ray crystallography.[6] Thus, we concluded that **3** was successfully generated photochemically from **10**. It is interesting to note that **3** afforded regioisomeric *syn*-[π12+π14] dimers **11** and **12**, while **2** gave stereoisomeric *syn*- and *anti*-[π8+π10] dimers; the preferential *syn*-dimerization may be rationalized by the extended secondary orbital interactions in the transition states characteristic to the naphtho-fused system. Compound **3** is, however, kinetically less stable than **2**, presumably reflecting the smaller HOMO-LUMO gap in **3** (Scheme 3).[7,8]

We next turned our attention to the theoretical studies of **3** to gain better understanding of this intriguing molecule. Nucleus-independent chemical shifts (NICS), recently proposed by Schleyer et al.,[9] have proven to be a simple and efficient probe of aromaticity:[10] negatively large NICS values denote aromaticity and the positively large values denote antiaromaticity, while small NICS values indicate nonaromaticity. Accordingly, NICS(1) values were calculated for a series of troponoid compounds **1**–**7** (Scheme 1) with the GIAO method at the RHF/6-31+G* level for B3LYP/6-31G* optimized geometries at points 1 Å above the ring centroids.[11,12] The results are summarized in Table 1, together with their calculated C=O bond lengths. Parent tropone **1** shows the NICS(1) value of −2.9, indicating little resonance stabilization in this system. Interestingly, the NICS(1) value of the tropone ring becomes more negative (more aromatic) when a tropone ring is fused at the 3,4-position to benzene (to form **2**) or naphthalene (to form **3**), whereas those of the fused benzenoid rings become more positive relative to the parent compounds. Thus, it seems that the aromaticity of the tropone rings of **2** and **3** is increased at the expense of that of the fused benzenoid rings. Particularly interesting is the finding that the NICS(1) value of the tropone ring in **3** (−7.4) approaches to that of benzene (−11.2), suggesting increased contribution of polarized resonance form **3b**. In sharp contrast, the corresponding values in **4**–**7** become more positive (less aromatic) and are closer to zero. The closely attended elongation of the C=O bonds of **1**–**7** with the enhancement in their negative NICS(1) values attests that the NICS(1) values properly reflect the contributions of the polarized resonance forms.

In conclusion, the NICS(1) values of **3** and related compounds indicate increased aromatic character of the tropone ring in **3** as compared to those of the lower homologues **1** and **2**, consistent with a substantial contribution of polar resonance structure **3b**. Experimentally, however, *o*-quinoidal **3** undergoes rapid [π12+π14] thermal dimerization even at low temperature. Further work aimed at kinetic stabilization of this system is in progress.

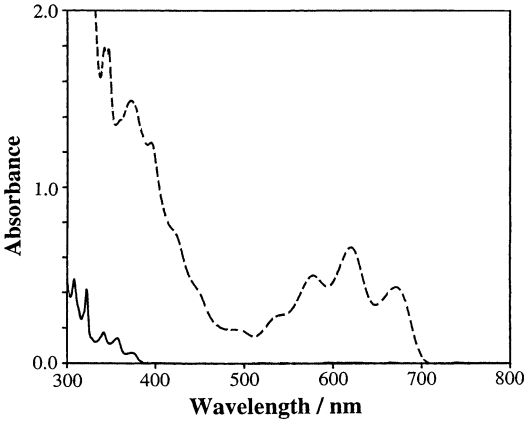
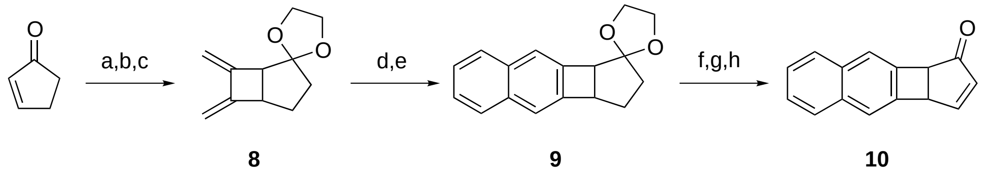
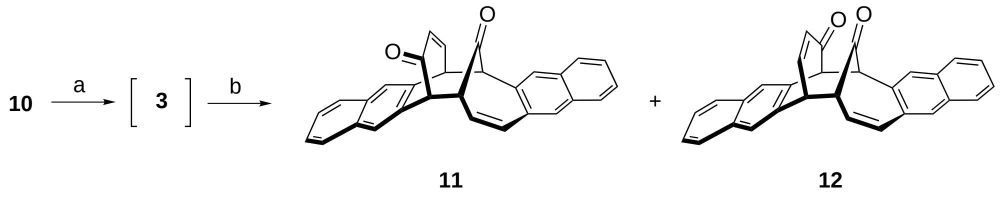


**Figure 1.** Absorption spectral changes observed upon irradiation of **10** with a high-pressure mercury lamp through Pyrex in EPA glass at −196°C: before irradiation (solid line) and after irradiation (dashed line; $\lambda_{max}$/nm 533sh, 577, 621, 674).



**Scheme 2.** (a) (*E*)-1,4-Dichloro-2-butene, *hν*, 12°C, 12 h, 58%; (b) ethylene glycol, TsOH, benzene, 80°C, 94%; (c) *t*-BuOK, 18-crown-6, THF, 94%; (d) *o*-dibromobenzene, *n*-BuLi, toluene, room temperature, 54%; (e) DDQ, benzene, room temperature, 85%; (f) $PyHBr_3$, dichloromethane, room temperature, 57%; (g) *t*-BuOK, 18-crown-6, THF, 84%; (h) aqueous 1N HCl, THF, room temperature, 80%.



**Scheme 3.** (a) $h\nu$/Pyrex, EPA, −196°C; (b) <−100°C.

**Table 1.** Calculated NICS(1) values and C=O bond lengths for compounds **1**–**7** (GIAO-RHF/6-31+G*//B3LYP/6-31G*).

| Compound | Ring-A | Ring-B | Ring-C | C=O bond length (Å) |
|---|---|---|---|---|
| **1** | −2.9 | – | – | 1.235 |
| **2** | −5.7 | −5.5 | – | 1.240 |
| **3** | −7.4 | −8.6 | −5.3 | 1.242 |
| **4** | −1.4 | −12.0 | – | 1.235 |
| **5** | −0.5 | −12.8 | −11.5 | 1.235 |
| **6** | −1.7 | −11.2 | – | 1.234 |
| **7** | −0.6 | −12.0 | −11.4 | 1.234 |

## Acknowledgements

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3. For 2,3-benzotropone (**4**): Colling, E. W.; Jones, G. *J. Chem. Soc. C.* **1969**, 2656.
4. For 4,5-benzotropone (**6**): (a) Thiele, J.; Weitz, E. *Ann.* **1910**, *377*, 1; (b) Föhlich, B. *Synthesis* **1972**, *4*, 564.
5. Spectroscopic data for **10**: $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.30 (d, $J$=3.0 Hz, 1H), 4.78 (dd, $J$=3.1 and 3.0 Hz, 1H), 6.09 (d, $J$=6.0 Hz, 1H), 7.40–7.46 (m, 2H), 7.56 (s, 1H), 7.70 (s, 1H), 7.75–7.80 (m, 2H), 7.85 (dd, $J$=6.0 and 3.1 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 51.16, 53.21, 121.32, 122.77, 126.02, 126.09, 128.60, 128.88, 134.13, 134.23, 134.29, 138.99, 144.03, 162.11, 205.47; IR (KBr) 1692, 760 cm$^{-1}$; UV (EtOH) $\lambda_{\max}$ 270 ($\varepsilon$ 13000), 278.5 (13000), 287.5 (8400, sh), 309 (960), 322 (880), 343 nm (330); MS (FD) $m/z$ 206 (M$^+$, 100); HRMS calcd for $C_{15}H_{10}O$ 206.0732, found 206.0740.
6. Crystallographic data for **11**: $C_{30}H_{20}O_2$, $M$=412.49, monoclinic, $C2/c$, $a$=38.3950(8), $b$=10.6826(8), $c$=20.3502(5) Å, $\beta$=94.6002(7)°, $V$=8319.9(7) Å$^3$, $D_{\text{calcd}}$=1.317 g cm$^{-3}$, $Z$=16, Mo-K$\alpha$ radiation, $T$=193 K, $\mu$=0.81 cm$^{-1}$. The final $R$- and $R_{\text{w}}$-values were 0.050 and 0.071, respectively, for 5992 reflections with $I$>3$\sigma I$ (independent 8978) and 577 parameters. For **12**: $C_{30}H_{20}O_2$·0.5ether, $M$=412.49, monoclinic, space group $P2_1/c$, $a$=7.6972(6), $b$=16.320(1), $c$=19.8920(8) Å, $\beta$=94.518(1)°, $V$=2491.0(3) Å$^3$, $D_{\text{calcd}}$=1.199 g cm$^{-3}$, $Z$=4, Mo-K$\alpha$ radiation, $T$=123 K, $\mu$=0.75 cm$^{-1}$. The final $R$- and $R_{\text{w}}$-values were 0.049 and 0.060, respectively, for 2793 reflections with $I$>3$\sigma I$ (independent 5636) and 334 parameters. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 164265 (for **11**) and CCDC 164266 (for **12**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
7. Compound **2** undergoes dimerization with the rate constant of 12±3 M$^{-1}$ s$^{-1}$ in EPA at −78°C and is relatively stable at −78°C ($t_{1/2}$ >300 s at the concentration comparable to that of **3** in the present investigation).[2] Compound **3** was too unstable to determine the rate constant for dimerization.
8. Calculated HOMO-LUMO gap (B3LYP/6-31G*) is 0.10502 a.u. for **2** and 0.07692 a.u. for **3**.
9. Schleyer, P.v. R; Maerker, C.; Dransfeld, A.; Hommes, N. J. R.v. E *J. Am. Chem. Soc.* **1996**, *118*, 6317.
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12. All the NICS values were calculated at points 1 Å above the ring centroids to minimize the interference from the local magnetic anisotropy due to the carbonyl group.