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2,3,6,7-Naphthalenetetracarboxylic dianhydride revisited

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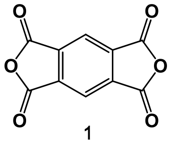
A B S T R A C T

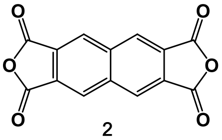
2,3,6,7-Naphthalenetetracarboxylic dianhydride was prepared and characterized by UV, IR, and NMR spectra. Its structure was confirmed by single crystal X-ray determination. It is a moderate strength electron acceptor, stronger than *p*-benzoquinone and weaker than pyromellitic anhydride according to quantum mechanical calculations and electrochemical measurements.

Pyromellitic dianhydride (**1**) is a well-known precursor of polyimides, which possess outstanding thermal and electrical properties, flame resistance, flexibility, and ability to coordinate transition metals.[1] Owing to their strong electron-accepting properties, both **1** and the respective diimides can serve as efficient acceptor components in both intermolecular and intramolecular charge transfer complexes with unusual photophysical and electrochemical properties.[2]

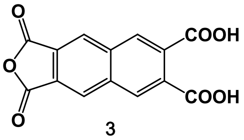
Although a relatively simple synthetic approach toward 2,3,6,7-naphthalenetetracarboxylic acid esters is known,[3] the properties of the corresponding dianhydride **2** are investigated to a much lesser degree. This compound has been mentioned as a subject of photochemical studies[4a] and as a precursor of the corresponding diimides,[4b,c] but mostly in the patent literature.[5] Moreover, the only available description of **2**[6] is somewhat contradicting. Thus, dianhydride **2** was described as a solid that darkens at about 400 °C without melting (mp <350 °C, according to[4b]) and was characterized by IR and UV absorption in water. These features do not fit to the structure of **2**, but may correspond to those of monoanhydride **3**. Whereas the condensation with amines, which is usually done at high temperatures, may be achieved using **2** contaminated with **3** or with **3** itself, the presence of **3** can have a detrimental effect on the yield in reactions such as Wittig reaction or its variation.[7] Therefore, we reinvestigated preparation of 2,3,6,7-naphthalenetetracarboxylic acid and its reaction with acetic anhydride and present here a detailed characterization of the pure dianhydride **2**.



1



2



3

Tetraethyl ester of 2,3,6,7-naphthalenetetracarboxylic acid was prepared following the known procedures.[8,3b] We found that basic hydrolysis described in[6] should be avoided, as acidification of the sodium and potassium tetraacid salt solutions always afforded mixtures of the tetraacid and the corresponding acidic salts that are poorly soluble in water, as evidenced by NMR spectra. However, hydrolysis of the ester with HBr in acetic acid afforded the pure tetraacid in 94% yield.[9] The tetraacid was converted into dianhydride **2** by refluxing in freshly distilled acetic anhydride. Formation of the dianhydride takes more time than that of pyromellitic anhydride. One-hour reflux[6] with eventual evaporation was apparently not sufficient. Removal of acetic acid formed in the reaction was beneficial for isolation of pure dianhydride **2** not contaminated by the acid.[10] The dianhydride crystallizes out from the reaction mixture as almost colorless needles, which sublime above 275 °C *without* decomposition. It is poorly soluble in toluene and moderately soluble in methylene chloride, acetone, and dioxane. A sample showing only one singlet at 9.16 ppm in acetone-d_6 rapidly reacted upon gentle warming with water present in DMSO-d_6 and, in addition to the singlet at 9.11 ppm, two singlets corresponding to monoanhydride **3** at 8.94 and 8.69 ppm became visible in the latter solvent.

The UV absorption spectrum (Fig. 1), in spite of its seeming complexity in the 270–380 nm range, can easily be deconvoluted using three Pekarian functions.[11] The resulting three vibronically split bands correspond to the transitions at 362, 348, and 283 nm, and a Gaussian-shaped strong band shows a maximum at 262 nm ($\varepsilon = 114{,}000$). The vibronic splitting of the first three absorption bands is in agreement with the highly symmetric structure of **2**.

Finally, the structure of **2** was confirmed by X-ray diffraction analysis[12] (Fig. 2). The symmetry of the molecule (C_i) deviates from the ideal (D_{2h}), owing to the presence of the short intermolecular C–H···O=C contacts (2.562 and 2.658 Å) observed for two of four hydrogen atoms. The effect of the strong electron-accepting substituents at the naphthalene moiety is seen mostly in shortening of the C3–C7 and C4–C5 bond lengths.

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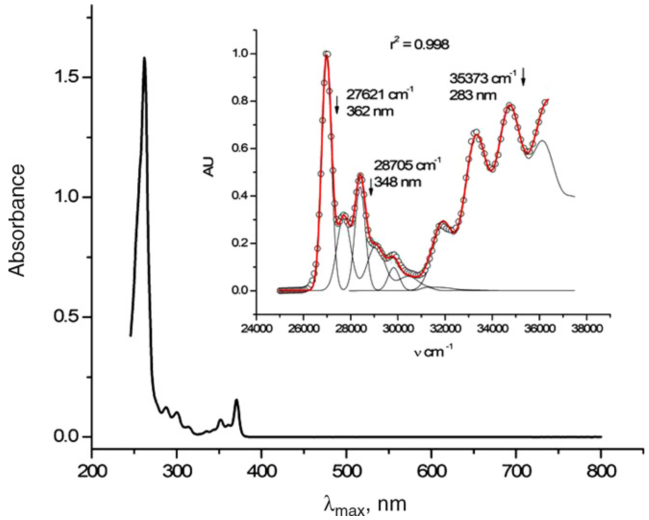

Figure 1. UV absorption of **2** in methylene chloride. Inset: circles—experimental spectrum, red curve—the sum of the three Pekarian curves.

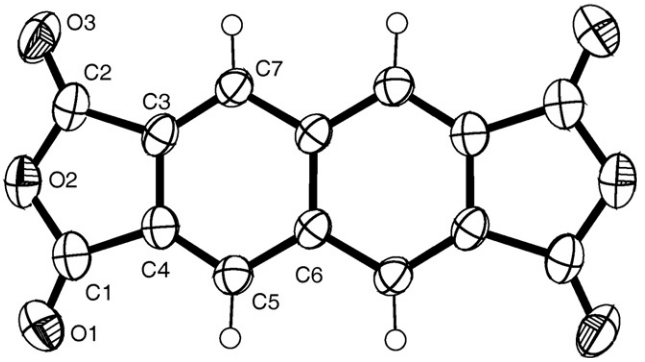

Figure 2. ORTEP plot of 2,3,6,7-naphthalenetetracarboxylic dianhydride **2** at 50% probability level. Selected distances in Å: O1–C1 1.187(3); C1–O2 1.394(3); O2–C2 1.339(3); C2–O3 1.185(3); C1–C4 1.475(3); C3–C4 1.410(3); C2–C3 1.480(3); C3–C7 1.361(3); C4–C5 1.357(3); C5–C6 1.420(3); C6–C6' 1.438(4); C6'–C7 1.423(3).

It is noteworthy that the observed molecular geometry of **2** is well reproduced by quantum mechanical calculations (B3LYP/6-31G(d,p) method).[13] The calculated at the same level of theory value of vertical electron affinity of **2** (1.73 eV) is lower than the value calculated for **1** (2.13 eV), but still higher than calculated for *p*-benzoquinone (PBQ). Thus, both **1** and **2** should be considerably stronger electron acceptors than PBQ. This conclusion contradicts to the accepted values of the electrochemical reduction potentials for **1** (−0.91 V vs SCE) and PBQ (−0.51 V vs SCE).[14] However, in our hands, the cyclic voltammetry in methylene chloride showed the first reduction peaks at −0.12 V for **1**, −0.36 V for **2**, and 0.50 V for PBQ (vs SCE, in methylene chloride) in agreement with the calculated electron affinities.

The absorption spectrum calculations in the gas phase using the TD B3LYP/6-31+G(d,p) method yielded only four allowed transitions of fourteen calculated: 340 ($f = 0.12$), 315 ($f = 0.01$), 265 ($f = 0.12$), 250 ($f = 1.5$) nm. Taking into account the solvent shift, the calculated absorption spectrum corresponds to the experimental (Fig. 1) very well.

We conclude that the formation of 2,3,6,7-naphthalenetetracarboxylic dianhydride from the respective tetraacid requires more drastic conditions than those used in the preparation of pyromellitic anhydride. The compound previously described as the dianhydride was, by all probability, not an individual compound. The problematic step in the previous preparations of **2** was basic hydrolysis of the corresponding tetra ester, which does not afford the salt-free tetraacid.

Acknowledgments

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9. ^{1}H NMR (DMSO-d_6, 250 MHz), δ: 8.15 (4H, s, CH), 13.32 (4H, s, OH).
10. *A typical procedure*: 2,3,6,7-naphthalenetetracarboxylic acid (1.0 g, 3.3 mmol) in freshly distilled acetic anhydride (60 ml) was refluxed for 10 h. Small amounts of acetic anhydride with acetic acid formed during the reaction were periodically distilled off and fresh portions of acetic anhydride were added to keep the reaction mixture volume constant. Pure dianhydride **3** (82%) crystallized upon cooling as almost colourless needles. ^{1}H NMR (acetone-d_6, 250 MHz), δ: 9.16 (4H, s, CH); ^{13}C NMR (acetone-d_6), δ: 163.27 (CO), 139.95 (CCC), 130.92 (CCO), 130.16 (CH). IR (nujol): 1868 (sh), 1842, 1828, 1807, 1778 cm^{-1} (C=O).
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12. Data were collected on Bruker-Nonius KappaCCD diffractometer with Mo Kα radiation, $\lambda = 0.71073$ Å. $C_7H_2O_3$. Unit cell parameters: *a* 15.745(1), *b* 5.1607(3), *c* 14.702 (1), $\beta = 118.929(4)$; space group *C*2/*c*. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 689964.
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