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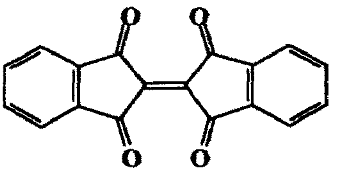
A New Strong Electron Acceptor. The Resurrection of 2,2'-Biindanylidene-1,3,1',3'-tetraone (BIT)

Vladimir Khodorkovsky*, Arkady Ellern and Ojars Neilands*[a)]

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, 84120 (Israel)
[a)]Department of Organic Chemistry, Riga Technical University, Riga, LV1658 (Latvia)

Abstract: Oxidation of 2,2'-biindan-1,3,1',3'-tetraone leads to 2,2'-biindanylidene-1,3,1',3'-tetraone, which structure has been unequivocally established.

A dimer of 1,3-indandione, 2,2'-biindanylidene-1,3,1',3'-tetraone (BIT) (1) has attracted attention of chemists about 100 years ago due to its expected dye properties (an analog of indigo). V. Kaufmann[1] isolated four products of oxidation of 1,3-indandione and assigned the structure 1 and the name "indenigo" to one of red products, which appeared later to be 6,11-dihydroxy-5,12-naphthacenedione 2.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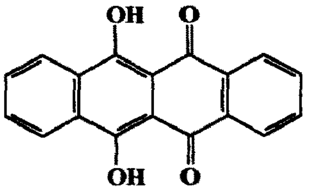
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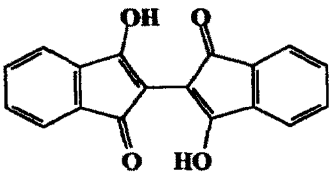
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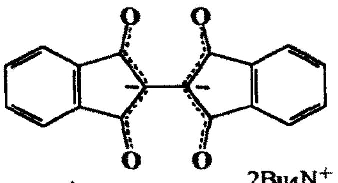

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Pursuing the same target molecule, G. Vanags[2] has obtained blue-violet trans-bis(bindonylene). BIT was supposed later to be the product of the reaction of 2-ethoxycarbonyl-1,3-indanedione with thiouracil (m.p. 207°)[3]. A. Schönberg reported[4] the formation of BIT from 2,2-dichloro-1,3-indanedione and copper (m.p.269-271°, red needles), but later G. A. Russel was unable to repeat this procedure[5]. A few years later the same author described[6] the synthesis of BIT from 2,2'-dibromo-(2,2'-biindane)-1,1',3,3'-tetraone in 7% yield. BIT was shortly described as red-brown needles, m.p. 270-271° (dec., orange color from 250°), λ_{max} in benzene 384 nm, ε = 13,200. The reaction of an adduct of 1,2,3-indantrione and 1,3-indandione with trifluoroacetic acid was also reported to afford 1 in 80% yield (249-251°,dec., λ_{max} in acetonitrile 278 (4.79), 344 (4.15))[7].

Our interest in this derivative stems from the assumption (confirmed by quantum-chemical calculations) that although there are no visible reasons to expect intensive color (no donor chromophore is present), BIT should possess strong electron acceptor ability itself and be a parent compound for a series of other acceptors by further modification of carbonyl groups in the same way as the modification of p-benzoquinone molecule leads to such important in the field of organic conductors components as tetracyano-*p*-quinodimethane and N,N-dicyano-*p*-quinodiimine. Another important feature of this molecule is that its carbon backbone presents a fragment of Buckminsterfullerene C_{60} and BIT may be used for the chemical synthesis of C_{60} and analogs.

We have failed to reproduce any of published procedures for the synthesis of BIT and only the formation of small amount of red **2** was eventually observed. At the same time, the reaction of a suspension of 2,2'-biindan-1,3,1',3'-tetraone (**3**) with dichlorodicyano-p-benzoquinone in acetonitrile leads smoothly to the desired BIT in a high yield (90-92%). BIT crystallizes from toluene as *almost colorless small needles, pink in the transient light* and sublimes at temperatures higher that 280° *without noticeable decomposition*. BIT crystallizes also from dichlorobenzene and propylene carbonate as pink big heavy needles. UV spectra in dichloroethane exhibit not only two strong absorption bands at 282 (ε = 39,820) and 349 nm (ε = 14,100), but also a weak broad one at 560 nm (ε = 40)[8]. A crystal suitable for X-ray structure has been grown from propylene carbonate. According to X-ray structure data[9] the molecule of BIT is bent along the C2...C9 and C11...C18 axes (Fig. 1), and possess a "chair" conformation, formed by three fragments I, II and III, planar within 0.008, 0.05 and 0.007 respectively. The bond lengths and angles are close to that observed in 1,3-indandione[10] and 3-(1',3'-indandione-2'-ylidene)-indanone (bindone)[11] and 2-dicyanomethylene-1,3-indandione[12] Astonishingly, no considerable strain due to the interactions of neighboring oxygen atoms is observed (distances O1...O3 and O2...O4 are 2.803(8) and 2.810(8) respectively and are longer then doubled van-der-Waals radius of oxygen atom - 2.54[13]). The oxygen atoms O1, O2, O3 and O4 deviate from the planes on 0.14, -0.48, 0.23 and -0.55A in the way, observed for bindone and 1,3-indandione itself[10,11] The crystal structure (Fig. 2) is characterized by relatively loose packing and no shortened intramolecular contacts are observed.

The cyclic voltammetry (CV) studies were somewhat limited by the low solubility of BIT at ambient temperature. Two reversible reduction waves are detectable at 0.07 and -0.30V in toluene-DMF mixture and at -0.08 and -0.28V in acetonitrile[14]. Scanning between -0.5 and +0.8V revealed an irreversible oxidation wave at +0.45V. For comparison, tetrabutylammonium salt **4** have been prepared from **3**[15]. CV oxidation of **4** at the same conditions as the reduction of **1**, afforded essentially the same results, confirming the existence of a reversible process:

$$\mathbf{1} \overset{+e^-}{\rightleftharpoons} \mathbf{1}^{\dot{-}} \overset{+e^-}{\rightleftharpoons} \mathbf{4}$$

BIT can be thus considered as a parent derivative for a series of new reversible two-stage one-electron redox systems with strong acceptor properties and is a promising candidate as an acceptor component of conducting donor - acceptor complexes. Although recently tetra(dicyanomethylene) derivative of BIT has been shown to be highly twisted[16], vinylogous tetraketone **5** is planar[17] and bi(dicyanomethylene) analog **6**

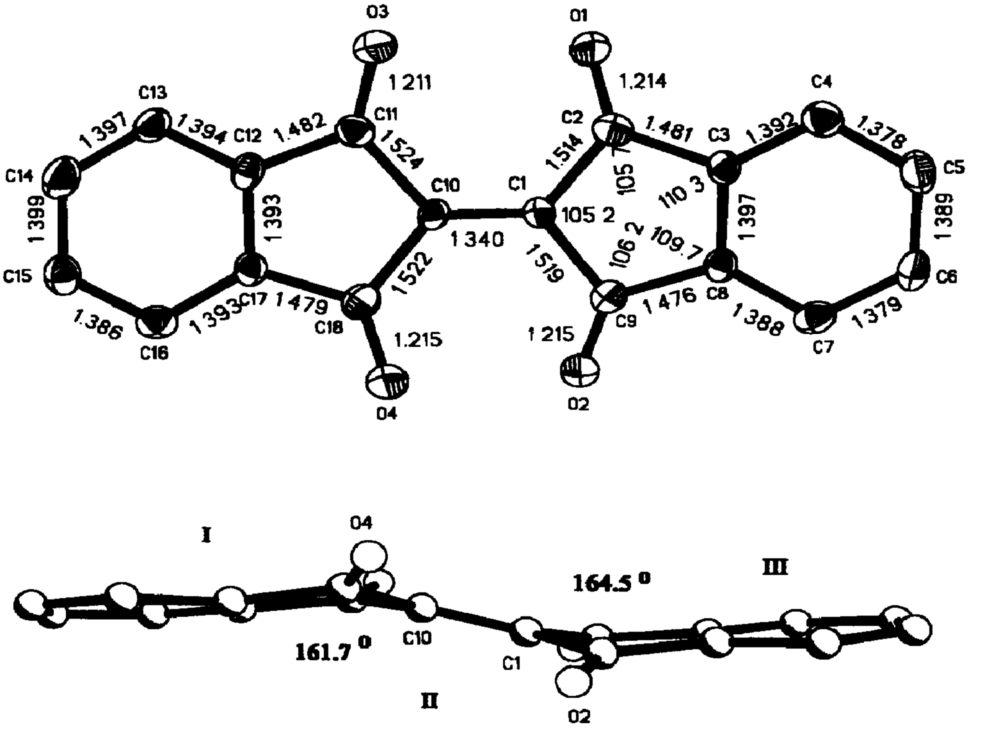


Fig. 1. Molecular structure of BIT (1).

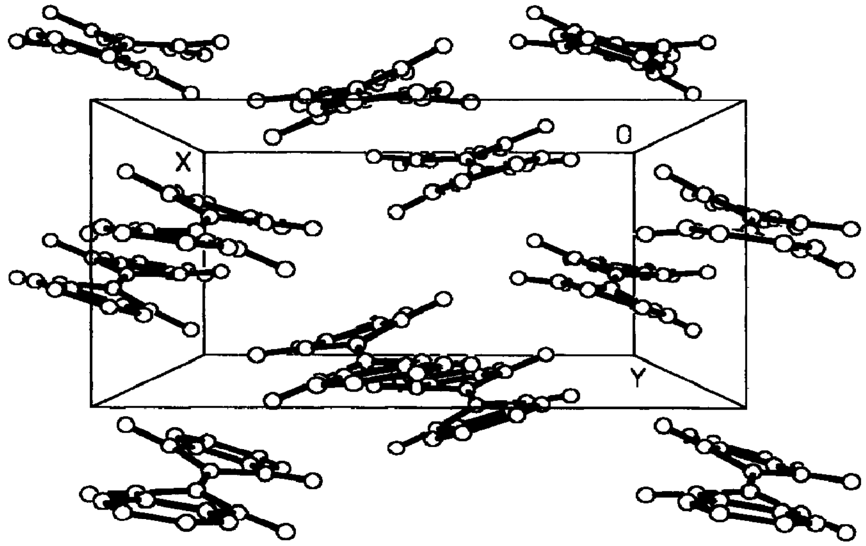
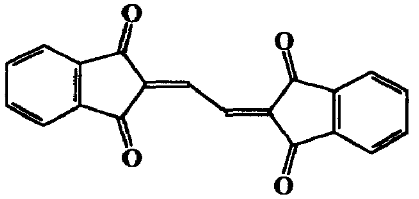


Fig. 2. Crystal structure of BIT (1).

exhibits two reversible reduction waves at 0.08 and -0.10V in benzonitrile[14,17].



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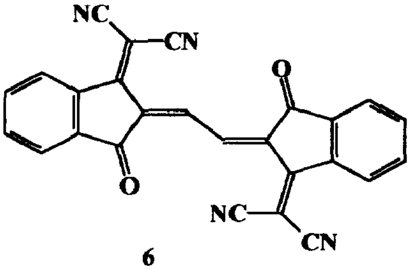

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Both BIT (**1**) and **6** form complexes with tetrathiafulvalene and other electron donors. Their structures and electrophysical properties are currently under investigation.

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8. IR spectra of **1** exhibit usual features of 1,3-indanedione derivatives: strong bands at 1729, 1698, 1673, 1240, 744, 729 cm^{-1} (in KBr).
9. X-Ray data for a single crystal of BIT (**1**) (size 0.35x0.21x0.14); $C_{18}H_8O_4$, M=288.2, orthorhombic, space group *Pbca*; at 153K, a = 12.781(5), b = 6.895(2), c = 27.909(9) , V = 2459.4(13) $Å^3$, Z=8, ρ_c = 1.557 Mg/m^3, $\mu(MoK\alpha) = 0.111mm^{-1}$, F(000)=1184. 1351 independent reflexions were measured with "Syntex P$\bar{1}$" diffractometer [$\alpha(MoK_\alpha)$ = 0.71069 , graphite monochromator, $\omega/2\theta$ - scan, $2\theta<42^o$] of which 903 were observed with $F_o>4\sigma(F_o)$. The structure was solved by direct method and refined by the least-square method in anisotropic approximation to R = 4.93, R_w = 4.28, GOF = 1,72, using a weighting scheme $\omega^{-1} = \sigma^2(F) = 0.0001F^2$. All calculations were carried out using the SHELX - 76 and SHELX-86 programs. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.
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15. Compound **3** was dissolved in 10% Bu_4NOH, evaporated in vac., washed with acetone and crystallized from acetonitrile-ethylacetate mixture to afford bright-red crystals. IR (strong bands): 2960, 2875 (hexachlorobutadiene), 1602, 1534, 876, 728 cm-1 (nujol).
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