Self-Condensation of 1,3-Indandione: A Reinvestigation

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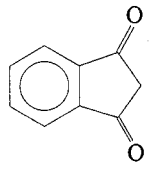
The self-condensation of 1,3-indandione and bindone in pyridine and acetic anhydride has been reinvestigated. The structures of a number of products have been determined by analysis of their NMR spectra and by X-ray structure determination.

Introduction

The ease of self-condensation of 1,3-indandione (**1**) was noticed as soon as it was synthesized in 1887.[1] Several products have been isolated in both basic and acidic conditions.[2] Whereas the structures of two of them, 1-(indan-1,3-dione-2-ylidene)indan-3-one (bindone, **2**) and tribenzo[*a,f,k*]trindenone (truxenequinone, **3**),[3] have been unequivocally established (the X-ray structure for **2** was reported[4]), the chemical identities of the other products have been either controversial or have never been verified using contemporary methods of chemical analysis.



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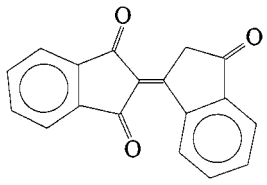

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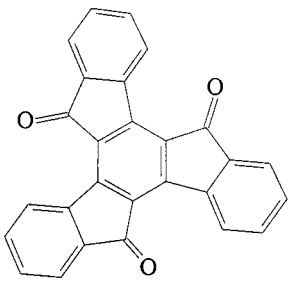

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Derivatives of 1,3-indandione are important intermediates in the synthesis of ninhydrins.[5] Recently, the interest toward 1,3-indandione has been renewed since it can serve as a potential precursor for the chemical synthesis of C_{60} and polyaromatic bowl-shaped hydrocarbons related to the fullerenes, e.g., via **3**.[6] Also, 1,3-indandione-2-ylidene and bindonylene moieties are promising electron accepting groups for push-pull conjugated systems with photochemically switchable second harmonics generation.[7] Recently we have demonstrated that 2-(cyclohexa-2′,5′-dienylidene)indane-1,3,4′-trione[8a] and 2,2′- biindanylidene-1,3,1′,3′-tetraone[8b] exhibit strong electron acceptor properties close to those of chloranil for the latter compound.

In this paper we report the results of our reinvestigation into the self-condensation of **1** and **2**. The structures of most synthesized products have been proven by X-ray structure analysis and NMR spectroscopy as well as by further chemical transformations.

Results and Discussion

Our first experiments on the self-condensation of **1** and **2** in pyridine have already shown that the reactions reproducibly lead to the formation of three products, described previously, see ref.[9] and references therein. Thus, refluxing **1** in pyridine resulted in the precipitation of **3** and the filtrate, after acidification and chromatographic separation, afforded two additional products. The use of chromatographic separation can be avoided by addition of methanol to the reaction mixture. One of the products was previously suggested as bis-bindone (**4a**),[9] and the second one as iso-

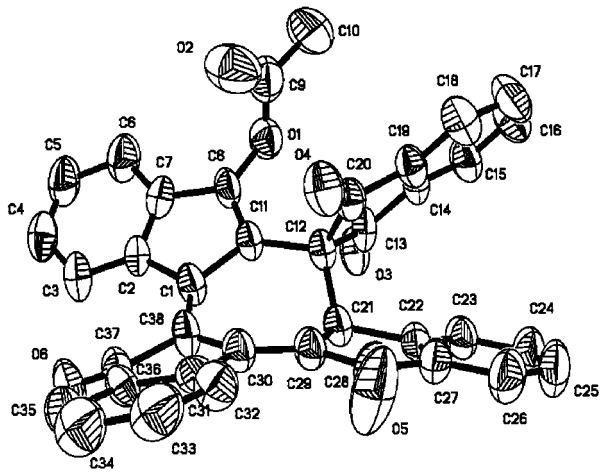

Figure 1. ORTEP diagram of the structure of **6** at 50% probability level

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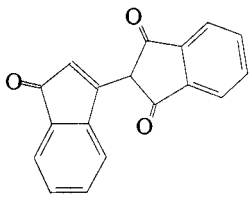
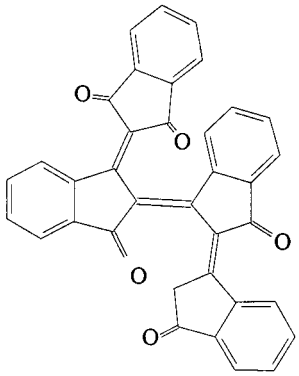
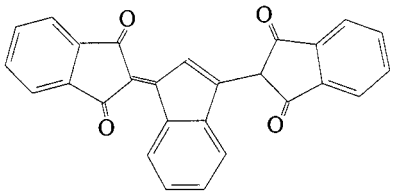


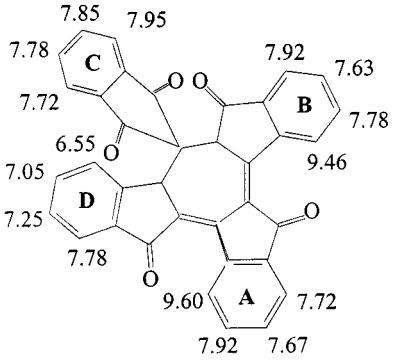
2a



4a



5a



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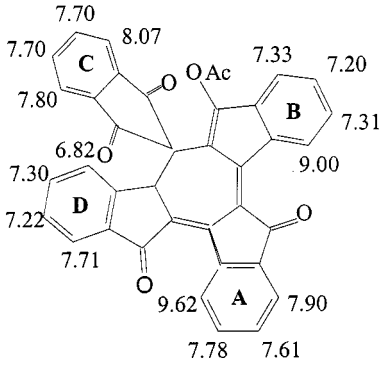

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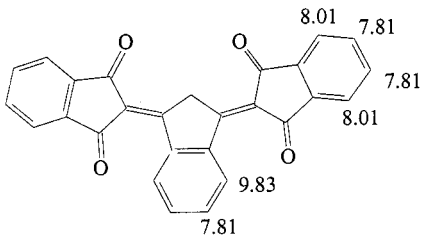

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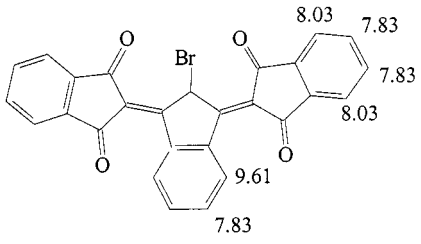


7

bindone (**2a**).[9,10] Later, structure **2a** was excluded and structure **5a**[11] was proposed. However, the NMR spectra that we obtained for both products were not consistent with the proposed structures. Acetylation of the first product, which was isolated from the filtrate in refluxing acetic anhydride followed by slow evaporation of the solution, afforded orange crystals of **6**, as evidenced by X-ray structure determination. Unexpectedly, the structure involved a seven-membered ring (Figure 1) and, therefore, the actual structure of **4a** corresponds to **4**, in full agreement with its NMR spectra. The second derivative, presumably **5a**,[11] was brominated to form a monobromo derivative. This derivative was crystallized from chloroform with one molecule of solvent and was proved to be 2-bromo-1,3-[bis(1,3-indandione-2- ylidene)]indane (**7**, Figure 2). Therefore, in full accordance with its ^{1}H NMR spectra, the previously suggested **5a** is actually 1,3-[bis(1,3-indandione-2-ylidene)]-indane (**5**).

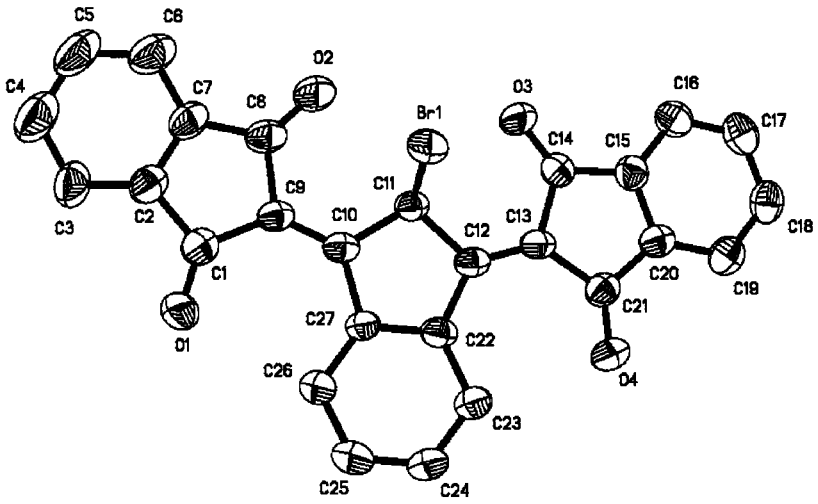


Figure 2. ORTEP diagram of the structure of **7** at 50% probability level

Further studies on the self-condensation reactions of **1** and **2** showed that derivatives involving four and even six indane fragments can form under certain conditions. It is noteworthy that elemental analysis data were not distinctive even for determining the number of indane moieties, since the difference in the C and H content for derivatives involving a close number of indane units (e.g., 3 and 4 or 5 and 6) was close to the experimental error. Mass spectra of some derivatives exhibit only peaks corresponding to the subsequent loss of carbonyl groups whereas peaks related to the molecular ions could not be detected in most cases. Therefore, for unequivocal identification of other products, we focused on analysis of their NMR spectra and X-ray structure determination.

NMR Spectral Analysis

A careful analysis of the NMR spectra of the compounds with known X-ray structures allowed us to reveal "fingerprints" of various substituted indane fragments, i.e. the most characteristic behavior of aromatic protons in different surroundings, and to apply this information for structure assignments of other products where X-ray measurements were not available.

In general, most aromatic protons in the spectra of all compounds studied have signals in the narrow chemical shift range of $\delta = 7-8$. All spectra involve a superposition of several (2 to 6) four-spin systems of aromatic protons. The use of a 500 MHz spectrometer enabled us to observe first-order spectra consisting of two doubled doublets and two doubled triplets with *ortho* spin-spin couplings of 7.6−8.0 Hz, and *meta*-splitting of 0.8−1.3 Hz for most of the unsymmetrically substituted aromatic rings. 2D COSY spectra allowed us to assign each signal of each four-spin system for compounds containing 4 and 6 moieties derived from **1**. In several cases (compounds **2**, **5**, **8**, etc.) the number of peaks in some multiplets and the splitting patterns do not correspond to first-order spectra. In those cases, a four-spin system simulation was performed and the best agreement of experimental and calculated spectra was observed when the chemical shift difference between two or three protons is 0−0.03 ppm. An example of such a simulation is shown in Figure 3 for the signal at $\delta = 9.16$ in the ^{1}H NMR spectrum of compound **8**.

The proton spectrum of indandione itself shows an AA′BB′ spin system with chemical shifts at $\delta = 8.02$ and 7.87. As a rule, in the 1,3-indandione fragments substituted only at the 2-position, the aromatic protons are found in a narrow chemical shift range of 0.2−0.4 ppm. The appearance of such four-spin systems, which in most cases give complex second-order spectra, indicates the presence of a 1,3-indandione unit. The consistent pattern of the chemical shifts in the indane units allows one to draw some conclusions about the structure of compounds where substantial chemical shift deviations from this narrow range were observed.

One of the most remarkable features of the ^{1}H NMR spectra for all products but **1** is the large downfield shift observed for one (or two) aromatic proton signals. For example, in the spectra of **2**, one aromatic proton has a signal at $\delta = 9.69$, which is more strongly deshielded by about 1.7 ppm than the corresponding protons in 1,3-indandione. This phenomenon is due to the close proximity of this proton to the adjacent carbonyl group of the 1,3-indandione unit. The number of these low-field signals (one or two) is a good indication of the number of directly connected indanone moieties (two or three, respectively). On the other hand, high-field displacement of signals can also be used for structural analysis. It could indicate either the absence of the acceptor C=O group in close proximity to any aromatic proton, or that the aromatic proton falls under the influence of the shielding zone of ring current stemming from the closest indane fragment, as in **4**, for instance.

The assignment of the ^{1}H NMR spectra for **4** and **6** was made as follows: two low-field signals in every spectrum ($\delta = 9.60$ and 9.46 for **4**, and $\delta = 9.62$ and 9.00 for **6**) belong to the protons that are in close proximity to the C=O group. Use of the 2D COSY technique allows us to assign all protons in such aromatic rings. The considerable

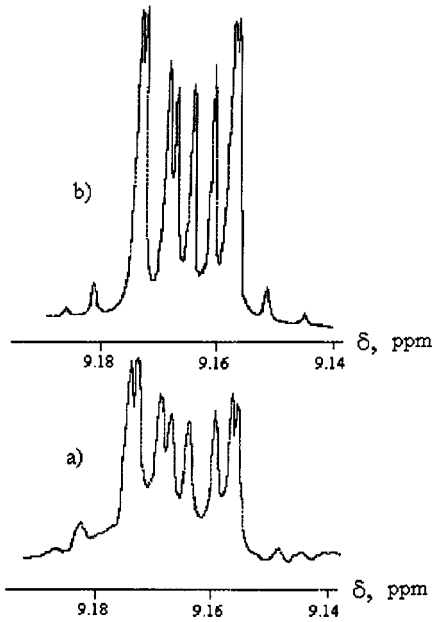


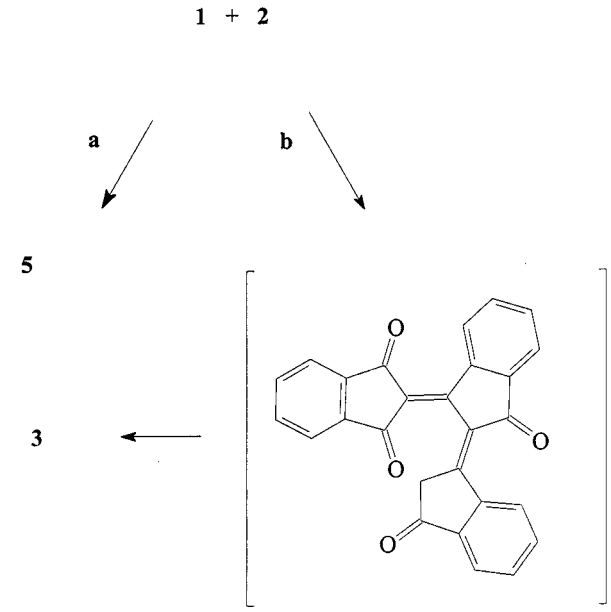
Figure 3. Experimental (a) and calculated (b) low-field multiplets of **8**

shielding effect for all protons in one of them, resulting from the conversion of a carbonyl group into a vinyl acetate group on going from **4** to **6**, allows us to assign these four-spin systems to units B for both compounds. The protons of units A in **4** and **6** are much less affected by acetylation. For both compounds the protons of the indandione moiety C give rise to four signals in a narrow chemical shift range (δ = 7.72−7.95 for **4** and 7.80−8.07 for **6**). The remaining signals in both spectra belong to protons of units D. The considerable high-field shift of one *ortho* proton in unit D (δ = 6.55 for **4** and δ = 6.82 for **6**) leads to the conclusion that it is situated in the anisotropic shielding area caused by the phenyl ring current of moiety C.

The relative simplicity of the spectra of **5**, the presence of a two-proton singlet at δ = 5.22 and the absence of signals integrated as one proton, undoubtedly rule out structure **5a**.

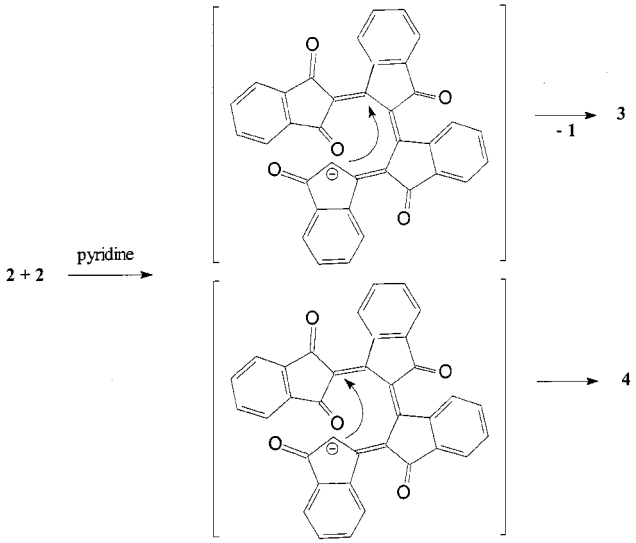
Furthermore, the presence of an acidic methylene group in compound **5** explains its facile bromination to give the monobromo derivative **7**.

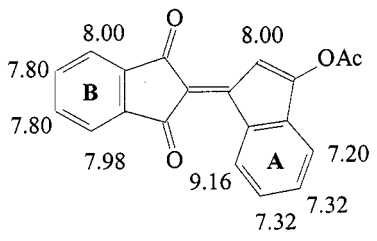
The reaction of indandione **1** with bindone **2** is represented in Scheme 1. The condensation can take place either at a carbonyl group of **2**, to yield **5** (path a), or at its methylene group (path b) to form the acyclic intermediate **3a** followed by cyclization to afford the final product, truxenequinone **3**. The condensation of two bindone molecules presumably gives a sterically constrained four-unit intermediate, as shown in Scheme 2. There are two ways to decrease the constraints: (a) forming truxenequinone **3** by releasing one molecule of indandione, and (b) immediate cyclization of the intermediate to form product **4**, which contains a seven-membered ring. According to the relative yields of **3** and **4**, the latter pathway is favored. Formation of **3** from **2** can also be rationalized in terms of a retro-aldol reaction.



3a

Scheme 1. Formation of **3** and **5** from indandione and bindone





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Scheme 2. Formation of **3** and **4** from two bindone molecules

Indeed, the reactions of **1**, **2** and mixtures of **1** and **2** lead to similar yields of **3**, **4** and **5**.

Self-Condensation in Acetic Anhydride

The self-condensation of **1** in pyridine proceeds as an aldol condensation with elimination of water, where the pyr-

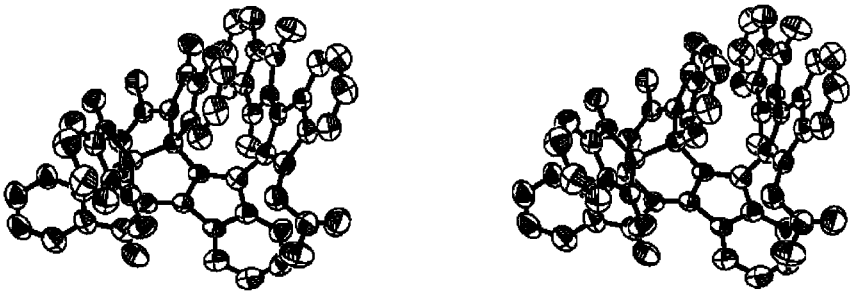
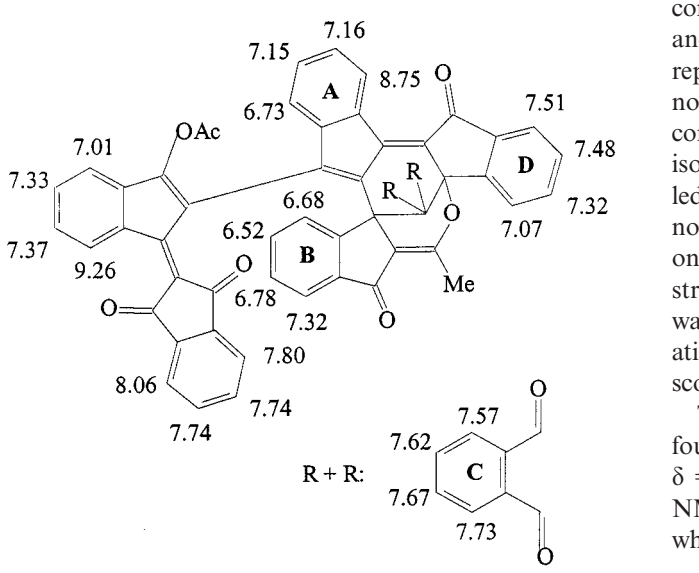


Figure 4. ORTEP diagram of the structure of **9** at 50% probability level

idine serves as a basic catalyst. The elimination of water upon self-condensation of **2** causes the retro-aldol reaction and this accounts for the formation of the same three products (**3**−**5**), as in the case of **1**. Such reactions should involve the formation of reactive enolic forms as intermediate species.

In order to trap such possible intermediates, the condensation reaction was carried out in acetic anhydride. Indeed, refluxing **1** in that solvent led to the formation of the acetyl derivative of the bindone enolic form **8** in 20−25% yields. Derivative **8** converts slowly into bindone (**2**) in the open air. This conversion proceeds quickly and quantitatively in a pyridine/water mixture. In some experiments, formation of small amounts of unidentified red solid was also observed. This compound turned yellow in a few hours in the open air, apparently reacting with moisture. The reaction was instant when the solid was dissolved in wet pyridine and derivative **3** precipitated as the only product. The compound was presumably the acetylated enolic form of **3a** and was not studied further since its formation was poorly reproducible. Surprisingly, the formation of derivative **6** was not detected, indicating that **4** is not formed under these conditions. However, two other products, **9** and **10**, were isolated from the reaction mixture. To the best of our knowledge, neither of these has ever been reported before. It is noteworthy that a red product mentioned in ref.[9] could be one of these products (or rather a mixture of the two). The structure of derivative **9** involves six indane moieties and was proved by X-ray determination (Figure 4). Other derivatives were carefully studied by ^{1}H- and ^{13}C NMR spectroscopy.

The ^{1}H NMR spectrum of compound **8** consists of two four-proton aromatic systems, one one-proton singlet at $\delta = 8.00$ and one three-proton singlet at $\delta = 2.41$. The ^{13}C NMR spectrum shows signals at $\delta = 166.56$ and $\delta = 21.36$, which belong to the acetoxy group, and two signals at $\delta =$



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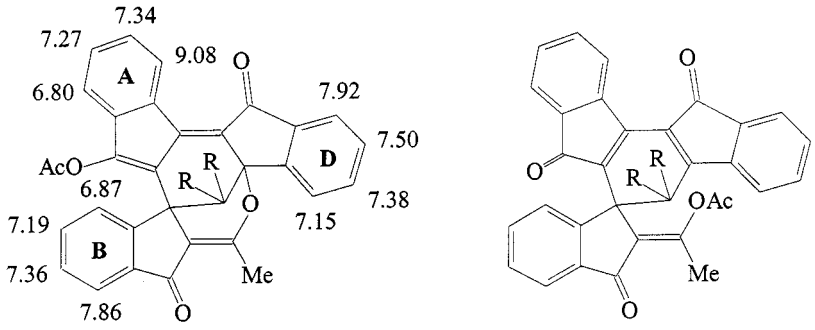
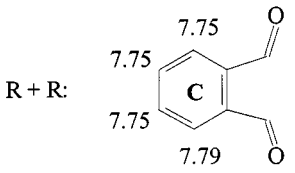


10 **10a**



110.49 and δ = 161.36, corresponding to carbons of an endocyclic double bond. The presence of a low-field signal at δ = 9.16 suggests that **8** involves a bindone fragment. Acetylation of the enolic form of bindone does not affect the proton chemical shifts in ring B, but those of ring A are shifted considerably to a higher field in comparison with similar protons in bindone. The largest high-field shift (0.78 ppm) is observed for the proton closest to the acetoxy group. The influence of the acetoxy group can also be noticed in the ^{13}C NMR spectrum by shielding the neighboring carbon in the benzene ring, causing a shift in the signal from δ = 123 to δ = 119.

The ^{1}H NMR spectrum of compound **9** consists of six four-spin systems of aromatic protons and two three-proton singlets. Comparison with the spectrum of **8** allows one to distinguish the proton signals of the acetylbindone moiety. They do not show considerable variations in the chemical shifts. The remaining resonances were analyzed as follows: the signals of ring A were characterized by the COSY spectrum on the basis of the observed lowfield signal of one *ortho*-proton (δ = 8.75). The doublet at δ = 6.68 belongs to the proton of ring B located in the shielding area of the aromatic ring in unit C. Four protons in the narrow chemical shift range δ = 7.57−7.73 belong to the 1,3-indandione ring C. The remaining four signals are ascribed to ring D.

The X-ray structure (Figure 4) of **9** shows that in the most favorable conformation of this molecule the planes of the acetylbindone moiety and ring B are almost parallel and spatially very close to each other. This may account for the essential change of chemical shifts of the protons in ring B, owing to a strong steric and anisotropic influence exerted by the neighboring acetylbindone fragment. Also, an important spectral feature of compound **9** is the presence of an exocyclic double bond, which results from the condensation of a methylene group with an acetoxy group. The carbon signals of this group in the ^{13}C NMR spectrum appear at δ = 163.6 and δ = 105.7.

The ^{1}H NMR spectrum of compound **10** shows the presence of four indandione-derived units (16 signals due to aromatic protons) and two singlets (each of 3 H) at δ = 2.53 and δ = 1.45. The unsymmetrical structure of the compound is proved by the fact that all 16 aromatic protons give separate signals. The presence of four aromatic units and only one low-field doublet (δ = 9.08) suggests that the molecule has only one bindone unit (A and B). Their protons were assigned by a COSY spectrum starting from the low-field doublet at δ = 9.08 and also from the doublet at δ = 6.87 (see above). The multiplet at δ = 7.75−7.79 belongs to indandione unit C, and the remaining signals to ring D. The presence of the exocyclic double bond is proved by the signals at δ = 164.2 and δ = 112.9 in the ^{13}C NMR spectrum.

The above considerations do not permit the distinction between two possible structural isomers, **10** and **10a**.

The COSY 2D NMR spectrum (Figure 5) shows that the doublets at δ = 9.08 and δ = 6.80 belong to the same spin system (ring A). The chemical shifts of the protons in the *peri*-position to the carbonyl group in all compounds

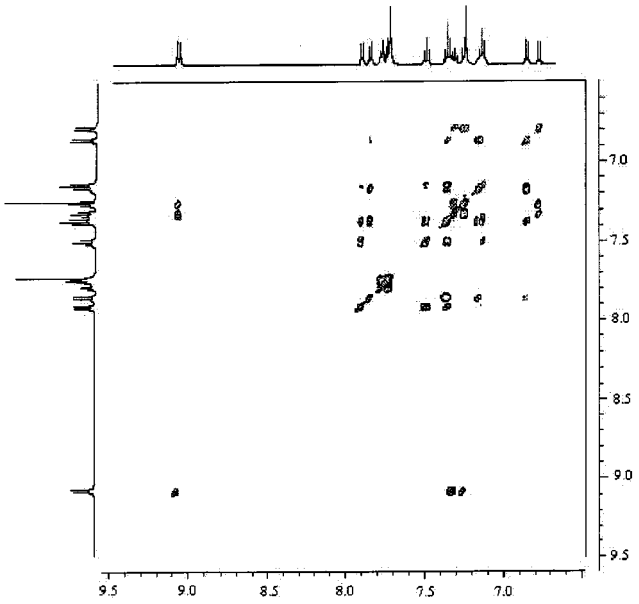


Figure 5. COSY 2D NMR spectra of **10**

studied are in the range δ = 7.6−8.0. This observed high-field resonance reflects the shielding effects of the acetoxy group and allows us to ascribe the bicyclo[3.3.1]oxanonadiene structure **10** to the compound rather than **10a**. Upon refluxing derivative **10** in pyridine, the acetyl group is removed followed by opening of the dihydropyran cycle and rearrangement of the double bonds, resulting in the formation of compound **11**. In the case of this compound, the doublet of the *peri*-proton possesses a chemical shift value of δ = 7.46. The same conclusion may be drawn by considering the ^{13}C NMR chemical shifts. In all compounds studied here, the proton-bearing aromatic carbons give signals in the range of δ = 123−136. In the case of compound **10** there is one signal at δ = 119.08, which is similar to the one in acetylbindone observed at δ = 119.00. Again, in the case of ring-opened product **11**, all aromatic protons fall within the range of δ = 123−136.

The same products (**8**−**10**) in essentially the same yields were obtained in the reaction of derivative **2** with acetic anhydride.

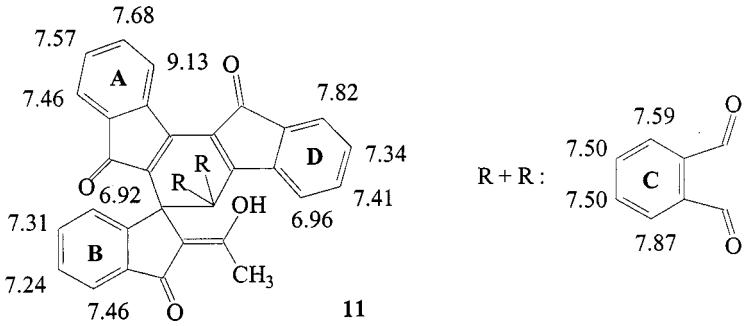
Self-Condensation in Pyridine/Acetic Anhydride Mixtures

A competition between two possible condensation pathways by refluxing **1** or **2** in a 1:1 mixture of acetic anhydride and pyridine results in the formation of **3** and **11**.

This structure was corroborated by comparison of its ^{1}H- and ^{13}C NMR spectra with those of **9** (see above), and by the fact that the hydrolysis of **9** in pyridine gave **11**.

Further Chemical Conversions

Most condensation products that were obtained in acetic anhydride undergo fast deacetylation and conversion into the derivatives formed in pyridine. Thus, acetylbindone **8** was refluxed in dry pyridine to afford a mixture of **3** and **4**. In the presence of water, this reaction at room temperature resulted in the quantitative formation of **2**, as mentioned



above. Refluxing derivative **10** in pyridine afforded **11**. Refluxing derivative **9** in pyridine led to the formation of a mixture of **11** and **3**, as a result of the release of the acetylbindone moiety and ring opening of the species bearing four indane units. Interestingly, the formation of the two-latter products was also noticed during self-condensation of bindone in the mixture of pyridine and acetic anhydride.

Experimental Section

General: Most of the products do not exhibit characteristic melting points and undergo slow decomposition depending on the heating rate. − NMR: Bruker AM 200 and Bruker AM 500; solvent $CDCl_3$; internal standard TMS. − IR: Impact 410. − UV-VIS: HP 89531A. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 117234, 117235, and 117236 for **6**, **7** and **9**, respectively. The SHELXTL [Bruker AXS, 1998] software package was used for calculations and drawings.

Self-Condensation of 1,3-Indandione in Pyridine: A mixture of indandione (2.00 g, 13.7 mmol) and 3 mL of pyridine was heated under reflux for 1 h. Methanol (25 mL) was added and the mixture was filtered. To the yellow solid obtained was added 15 mL of 10% methanolic KOH and the mixture was heated under reflux for 15 min. Filtration of the hot solution afforded yellow needles of **3**. The filtrate was acidified with concentrated HCl to give yellow crystals of **4**. A third yellow solid (**5**) was obtained by the acidification of the first filtrate. All the compounds were recrystallized from chlorobenzene. Yield of **3**: 0.53 g (32%), m.p. > 350 °C; yield of **4**: 0.64 g (35%), slow decomposition above 200 °C; yield of **5**: 0.55 g (30%), m.p. 326−328 °C.

Indandione 1: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.02 (m, 2 H), 7.87 (m, 2 H), 3.44 (s, 2 H, CH_2).

Bindone 2: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.69 (d), 7.82 (t), 7.87 (t), 7.98 (d), 8.03 (m), 7.99 (m), 7.83 (m, 2 H), 4.18 (s, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$, 125.77 MHz, low-intensity signals of quaternary carbons are marked by asterisks): δ = 200.99*, 191.05*, 189.42*, 156.84*, 155.38*, 145.88*, 141.66*, 141.25*, 140.40*, 135.38, 135.33 (2C), 134.16, 131.67, 123.50, 123.39, 123.05, 43.41.

Truxenequinone 3: IR (nujol, strong bands): $\tilde{\nu}$ = 1712, 1610, 1596, 1571, 1320, 1272, 1202, 1156, 1089 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.31 (d, 3 H), 7.72 (t, 3 H), 7.58 (t, 3 H), 7.87 (d, 3 H).

4: IR (nujol, strong bands): $\tilde{\nu}$ = 1712 cm^{-1}, 1693, 1677, 1645, 1613, 1562, 1482, 1322, 1281, 1242, 1140, 1092, 996, 920, 900, 868, 833, 801. − ^{1}H NMR ($CDCl_3$, 500 MHz), the signals of aromatic protons are given in the order of their belonging to four-spin systems of indandione units, as revealed by COSY 2D NMR; integral intensity of every signal corresponds to one proton unless stated otherwise: δ = 9.60 (d), 7.92 (t), 7.67 (t), 7.72 (d), 9.46 (d), 7.78 (t), 7.63 (t), 7.92 (d), 7.95 (d), 7.85 (t), 7.78 (t), 7.72 (d), 7.78 (d), 7.25 (t), 7.05 (t), 6.55 (d), 4.91 (s), 4.45 (s). − ^{13}C NMR ($CDCl_3$, 125.77 MHz, because of the very poor solubility most quaternary carbons were not observed): δ = 200.99*, 189.72*, 150.33*, 146.78*, 146.04*, 137.24*, 136.41, 136.20, 136.05, 135.34, 133.60, 132.75, 131.94, 130.77, 128.85, 128.53, 125.20, 124.27, 123.61 (3C), 123.01, 56.28, 49.40.

The yield of **5** can be slightly improved by shortening the reaction time. In a separate experiment, **1** (1.00 g, 6.85 mmol) and 3 mL of pyridine were heated under reflux for 15 min. After cooling and addition of 25 mL of methanol the mixture was filtered. The dark green colored filtrate was acidified with conc. HCl to give a brown-yellow solid. Recrystallization of this material from chlorobenzene afforded 0.32 g (35%) of **5** as bright yellow crystals. − IR (nujol, strong bands): $\tilde{\nu}$ = 1712 cm^{-1}, 1680, 1603, 1584, 1562, 1351, 1283, 1223, 1156, 1038, 983, 875, 811, 741. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.83 (m, 2 H), 8.01 (m, 4 H), 7.81 (m, 6 H), 5.22 (2 H).

Self-Condensation of Bindone in Pyridine: The above procedure was used for the reaction of bindone (2.00 g, 7.3 mmol) in 3 mL of pyridine. Heating the mixture under reflux (1 h) and subsequent workup afforded 0.52 g (28%) of **3**, 0.66 g (34%) of **4** and 0.61 g (31%) of **5**.

Self-Condensation of 1,3-Indandione and Bindone in Pyridine: The above procedure was used for the reaction of indandione (0.52 g, 3.6 mmol) and bindone (1.00 g, 3.6 mmol) in 3 mL of pyridine. Heating the mixture under reflux (1 h) and subsequent workup afforded 0.39 g (28%) of **3**, 0.49 g (34%) of **4** and 0.45 g (31%) of **5**.

Acetylation of 4: Compound **4** (0.25 g, 0.47 mmol) was heated under reflux in 5 mL of acetic anhydride for 1 h. The color became dark and, after cooling, red crystals of **6** precipitated. Recrystallization from acetic anhydride and slow evaporation afforded tiny orange plates of poor quality, which turned black above 170 °C. Yield 0.17 g (64%). − IR (nujol, strong bands): $\tilde{\nu}$ = 1772 cm^{-1}, 1704, 1593, 1261, 1181, 1091, 996, 891, 756. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.62 (d), 7.78 (t), 7.61 (t), 7.90 (d), 9.00 (d), 7.31 (t), 7.20 (t), 7.33 (d), 8.07 (d), 7.80 (m), 7.70 (m, 2 H), 7.71 (d), 7.30 (t), 7.22 (t), 6.82 (d), 5.10 (s), 1.47 (s, 3 H).

X-ray structure determination: a red plate of **6** ($0.2 \times 0.2 \times 0.1$ mm) was analyzed: $C_{38}H_{20}O_6$, triclinic, space group *P*-1, at 298 K, $a = 11.295(3)$, $b = 12.538(3)$, $c = 13.476(5)$ Å, $\alpha = 90.24(2)°$, $\beta = 112.16(2)°$, $\gamma = 103.22(2)°$, $Z = 2$, $V = 1711.9(9)$ Å^3, $F(000) = 592$. 4212 reflections were collected with a Syntex $P\bar{1}$ diffractometer [λ(Mo-K_α) = 0.711069 Å, graphite monochromator, $\omega/2\theta$-scan, $2\theta < 42°$]. 2398 reflections with $F_o > 4\sigma(F_o)$ were observed from 3961 independent reflections. The structure was solved by direct methods. In spite of the very low scattering and small reflection-to-parameter ratio the structure was successfully refined by least-squares in full-matrix approximation for nonhydrogen atoms: 418 parameters, $R = 0.101$, $Rw = 0.258$, GOF = 1.12. The hydrogen atoms were included in geometrically calculated positions and $U_{iso} = 0.08$ Å^2. The small size of a crystal and its poor quality led to comparatively high values of the *R*-factors.

Bromination of 5: Derivative **5** (0.40 g, 1 mmol) was dissolved in 50 mL of $CHCl_3$ by stirring at room temperature. A 20% solution of Br_2 in $CHCl_3$ was added dropwise until the color of bromine persisted. Evaporation of the solvent gave 0.55 g (92%) of **7** as yellow crystals (including chloroform as monosolvate − upon heating above 80 °C chloroform is lost and the compound decomposes above 230 °C). − IR (nujol, strong bands): $\tilde{\nu}$ = 1713, 1676, 1602, 1553, 1267, 1208, 1153, 1045, 722 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.61 (m, 2 H), 8.42 (s, 1 H), 8.03 (m, 4 H), 7.83 (m, 6 H).

X-ray structure determination: a yellow plate of **7** ($0.7 \times 0.3 \times 0.2$ mm) was analyzed: $C_{27}H_{13}BrO_4{\cdot}CHCl_3$, monoclinic, space group $P2_1/c$, at 298 K, $a = 9.686(2)$, $b = 23.077(6)$, $c = 11.036(2)$Å, $\beta = 100.35(2)°$, $Z = 4$, $V = 2426.7(9)$ Å^3, $F(000) = 1200$. 4073 reflections were collected with a Syntex *P*-1 diffractometer [λ(Mo-K_α) = 0.711069 Å, graphite monochromator, $\omega/2\theta$-scan $2\theta < 48°$. 2575 reflections with $F_o > 4\sigma(F_o)$ were observed from 3831 independent reflections. The structure was solved by direct methods and refined by least-squares in full-matrix approximation for nonhydrogen atoms: 381 parameters, $R = 0.0616$, $Rw = 0.1544$, GOF = 0.955. The hydrogen atoms were included with geometrically calculated positions and refined with the riding model.

Self-Condensation of Bindone in Acetic Anhydride: Bindone (2.00 g, 7.3 mmol) was refluxed in 5 mL of acetic anhydride for 45 min. On cooling, a red solid precipitated, which was purified by column chromatography on silica gel. Elution with CH_2Cl_2 gave three products (**8**−**10**). Yield of **8**: 0.53 g (23%), m.p.180−83 °C; yield of **9**: 0.74 g (35%), decomposes above 245 °C; yield of **10**: 0.22 g (10%), m.p. 175−177 °C. − **8**: IR (nujol, strong bands): $\tilde{\nu}$ = 1770 cm^{-1}, 1715, 1677, 1600, 1565, 1539, 1325, 1255, 1153, 1175, 1076, 990, 865, 744, 760. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.16 (m), 7.32 (m, 2 H), 7.20 (m), 8.00 (m), 7.98 (m), 7.80 (m, 2 H), 8.00 (s), 2.41 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 125.77 MHz, because of the poor solubility not all signals of quaternary carbons are observed): δ = 190.84*, 166.56*, 161.36*, 154.79*, 141.88*, 141.72*, 138.57*, 133.54*, 135.20 (2C), 131.32, 130.56, 129.63, 123.06, 119.00, 110.49, 104.86, 21.36.

9: IR (nujol, strong bands): $\tilde{\nu}$ = 1770 cm^{-1}, 1734, 1699, 1632, 1613, 1552, 1533, 1370, 1284, 1261, 1172, 1150, 996, 904, 868, 760, 737, 651. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.26 (d), 7.37 (t), 7.33 (t), 7.01 (d), 8.75 (d), 7.16 (t), 7.15 (t), 6.73 (d), 8.06 (d), 7.80 (m), 7.74 (2 H), 7.73 (d), 7.67 (t), 7.62 (t), 7.57 (d), 7.51 (d), 7.48 (t), 7.32 (t), 7.07 (d), 7.32 (d), 6.78 (t), 6.52 (t), 6.68 (d), 2.17 (s, 3 H), 2.10 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 125.77 MHz, because of the poor solubility not all signals of quaternary carbons are observed): δ = 206.80*, 198.55*, 192.26*, 191.73*, 190.56*, 190.02*, 170.34*, 166.86*, 163.62*, 154.57*, 152.20*, 149.60*, 147.17*, 145.10*, 144.92*, 144.39*, 142.71*, 138.73, 138.59, 137.98, 137.79 (2C), 137.77, 134.88*, 134.52, 134.03 (2C), 133.43, 132.76, 131.58, 131.07, 129.53, 129.49, 127.87, 127.06, 126.17 (2C), 125.92 (2C), 125.43, 123.39, 122.45, 105.75*, 20.54, 17.15.

X-ray structure determination: a deep red prism of **9** ($0.15 \times 0.15 \times 0.1$ mm) was analyzed: $C_{58}H_{30}O_9$, triclinic, space group *P*-1, at 298 K, $a = 11.228(1)$, $b = 13.555(1)$, $c = 14.092(1)$ Å, $\alpha = 99.56(2)°$, $\beta = 99.96(1)°$, $\gamma = 91.97(2)°$, $Z = 2$, $V = 2078.7(4)$ Å^3, $F(000) = 900$. 23608 reflections were collected with a Smart CCD diffractometer [λ(Mo-K_α) = 0.711069 Å, graphite monochromator, ω and θ-scan, $\theta < 28.4°$. 2363 reflections with $F_o > 4\sigma(F_o)$ were observed from 9988 independent reflections. The structure was solved by direct methods and refined by least-squares in full-matrix approximation for nonhydrogen atoms: 604 parameters, $R = 0.0809$, $Rw = 0.144$, GOF = 0.87. The hydrogen atoms were included in geometrically calculated positions and refined with the riding model.

10: IR (nujol, strong bands): $\tilde{\nu}$ = 1770 cm^{-1}, 1709, 1658, 1590, 1588, 1267, 1229, 1268, 1154, 1090, 904, 847. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.08 (d), 7.34 (t), 7.27 (t), 6.80 (d), 7.15 (d), 7.38 (t), 7.50 (t), 7.92 (d), 6.87 (d), 7.19 (t), 7.36 (t), 7.86 (d), 7.75 (m, 3 H), 7.79 (m), 2.53 (s, 3 H), 1.46 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 125.77 MHz, because of the poor solubility not all signals of quaternary carbons are observed): δ = 196.66*, 188.92*, 188.20*, 166.77*, 164.20*, 145.13*, 144.30*, 143.72*, 142.61*, 142.18*, 141.11*, 139.83*, 138.77*, 136.57, 136.24, 135.35, 132.66, 131.61, 130.86, 129.30, 128.92, 128.65, 125.86, 125.25, 124.62, 124.14, 123.44, 122.98, 119.09, 112.90*, 19.68, 17.46.

Self-Condensation of 1,3-Indandione in Acetic Anhydride: Indandione (1.00 g, 6.8 mmol) was refluxed in 5 mL of acetic anhydride for 45 min. On cooling, a red solid precipitated, and this was purified by column chromatography on silica gel. Elution with CH_2Cl_2 gave three products (**8**−**10**). The formation of a fourth, unidentified, product was observed in some experiments. The typical yields of products were somewhat lower than in the case of bindone: **8**: 17−20%; **9**: 28−34%; **10**: 7−10%.

Self-Condensation of Bindone in Acetic Anhydride/Pyridine Mixture: Bindone **2** (1 g, 3.6 mmol) was refluxed with 3 mL of acetic anhydride and 3 mL of pyridine for 1 h. Then 20 mL of methanol was added. On filtration a yellow solid was obtained, which was purified by column chromatography. On elution with CH_2Cl_2 the first fraction gave **3** (0.11 g, 12%). Further elution gave **11** (0.45 g, 44%) as yellow needles (m.p. 286−288 °C). − IR (nujol, strong bands): $\tilde{\nu}$ = 3411 cm^{-1} (br), 1709, 1661, 1595, 1570, 1267, 1229, 1207, 1153, 1090, 1005, 904, 847, 724. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.13 (d), 7.68 (t), 7.57 (t), 7.46 (d), 6.96 (t), 7.41 (t), 7.34 (t), 7.82 (d), 6.92 (d), 7.31 (t), 7.24 (t), 7.46 (d), 7.87 (m), 7.50 (m, 2 H), 7.59 (m), 1.94 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 125.77 MHz, because of the poor solubility not all signals of quaternary carbons are observed): δ = 197.50*, 191.24*, 141.44*, 140.74*, 140.03*, 135.57, 135.30, 134.31*, 134.22*, 133.45, 132.04, 131.58, 131.17, 130.21, 130.07, 129.55, 129.20, 128.45, 127.90, 126.57, 124.79, 124.52, 123.79, 104.95*, 24.22.

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