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Abstract

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ON THE STRUCTURE OF BINDONE AND ITS DERIVATIVES

Although anhydro-bis-indandione-1,3, or bindone ($\mathrm{I}, R = R' = H$), was synthesized long ago by Wislicenus (^{1}) and recently has found wide application as an analytical reagent for primary amines ($^{2-5}$) and nitro compounds (^{6}), the structure and possible tautomeric states of this compound and its derivatives have not been established in detail. By cleavage of dinitrobindone, Wislicenus (^{7}) obtained dinitromethane, which argues in favor of structure I. Fischer and Vanag (^{8}) obtained a second isomer of bindone, to which structure II was assigned. Recently, Zingewald (^{4}) again returned to the discussion of the possible structure of bindone on the basis of ultraviolet spectra.

To elucidate the structure and the state of individual functional groups in the molecules of bindone and some of its derivatives, we recorded the infrared and ultraviolet spectra and polarograms of these compounds; the results were compared with the corresponding data for derivatives of indandione-1,3 and indanone-1, since both of the above-mentioned rings enter into the bindone molecule.

(I) (II) (III)

In this work the following were studied: bindone ($\mathrm{I}, R = R' = H$), bromobindone ($\mathrm{I}, R = \mathrm{Br}; R' = H$), dibromobindone ($\mathrm{I}, R = R' = \mathrm{Br}$), methylbindone ($\mathrm{I}, R = \mathrm{CH_3}; R' = H$), bromomethylbindone ($\mathrm{I}, R = \mathrm{CH_3}; R' = \mathrm{Br}$), nitromethylbindone ($\mathrm{I}, R = \mathrm{CH_3}; R' = \mathrm{NO_2}$), nitrobromobindone ($\mathrm{I}, R = \mathrm{NO_2}; R' = \mathrm{Br}$), dinitrobindone ($\mathrm{I}, R = R' = \mathrm{NO_2}$), the monoxime of bindone, 2-(indanone-1′-yl-3′)-indandione-1,3 (III), isobindone (II), and the potassium salts of bindone and isobindone.

The IR spectra were recorded for the compounds in the solid state (suspensions of the substance in paraffin oil). The wave numbers and relative absorption values are presented in Table 1. The same table also gives the absorption maxima in the ultraviolet for $10^{-5} M$ solutions of the compounds in ethanol. Polarograms were recorded for 10^{-5}—$5 \cdot 10^{-5} M$ aqueous solutions of the compounds in Britton–Robinson buffers in the pH range from 2 to 11 against a background of 0.1 N KCl, and also in a 0.1N solution of K_2CO_3; the dependence of the half-wave potential ($E_{1/2}$) on pH is given in Table 2 in the form of equations. The $E_{1/2}$ values are referred to the saturated Hg_2Cl_2 electrode. The experimental work was carried out on IKS-14, SF-4 instruments and a Heyrovský polarograph.

It follows from the IR spectrum of bindone that in the solid state the compound exists in the triketone form (I). The frequencies 1687 and 1716 cm^{-1} may be assigned to carbonyl vibrations; of these, the first is associated with $C = O$ vibrations in the indandione ring, and the second with $C = O$ vibrations in the indanone ring. Owing to conjugation, the frequency 1687 cm^{-1} is strongly lowered not only in comparison with—

Table 1

Compound	Most characteristic frequencies, cm^{-1} (relative absorption values are given in parentheses)	UV absorption of alcoholic solutions, Å (values of $\varepsilon \cdot 10^{-4}$ are given in parentheses)*
2-(Indanone-1′-yl-3′)-indandione-1,3	1744 (61); 1711 (100); 1694 (99); 1608 (80)	
Bindone	1716 (88); 1687 (90); 1609 (75); 1592 (94); 1574 (98)	2245 (4,62); 2520 (4,35); 2750 (infl.); 3050 (1,58); 3555 (1,17); 5250 (1,38)
Methylbindone	1717 (85); 1680 (100); 1609 (70), 1582 (83); 1559 (94)	
Bromomethylbindone	1726 (90); 1689 (100); 1609 (33); 1560 (73)	2450 (2,42); 3480 (1,28); 4850 (0,22)
Nitromethylbindone	1740 (75); 1730 (74); 1688 (95); 1605 (28); 1589 (52); 1557 (100)	
Bromobindone	1719 (70); 1681 (80); 1656 (66); 1611 (59); 1550 (82)	
Dibromobindone	1732 (79); 1681 (90); 1609 (74); 1584 (68); 1550 (78)	
Nitrobromobindone	1749 (75); 1723 (74); 1691 (96); 1611 (49); 1572 (100)	2520 (3,91); 3500 (1,28); 5300 (1,10)
Dinitrobindone	1752 (90); 1730 (62); 1690 (100); 1601 (99); 1566 (86)	2200; 3000; 3570; 4840;
Bindone oxime	1724 (62); 1690 (99); 1608 (78); 1579 (100)	

Compound	Most characteristic frequencies, cm^{-1} (relative absorption values are given in parentheses)	UV absorption of alcoholic solutions, Å (values of $\varepsilon \cdot 10^{-4}$ are given in parentheses)*
Isobindone	1715 (35); 1681 (100); 1656 (42); 1606 (73); 1598 (87); 1575 (100); 1554 (51); 1452 (91)	2180 (3,28); 2680 (3,80); 3000 (infl.); 4200 (1,45); 6550 (1,05)
K salt of bindone	1663 (56); 1623 (63); 1581 (72); 1550 (43); 1483 (45)	
K salt of isobindone	1669 (46); 1623 (75); 1590 (84); 1554 (84); 1480 (99); 1440 (100)	

* The spectra were recorded 24 h after preparation of the solution.

compared with the frequency of C=O in indandione-1,3 (1710 cm^{-1}), and also compared with benzalindandione-1,3 (1696 cm^{-1}) (9). In the spectrum of indanonyl-indandione-1,3, where the double bond is hydrogenated, the frequency of the C=O group is normal (1711 cm^{-1}). The frequency 1716 cm^{-1}, compared with the normal frequency of vibration of C=O in the indanone ring (1698 cm^{-1}) (10), is elevated. That the first frequency is associated with the vibration of C=O in the indandione ring of the molecule is indicated by the constancy of this frequency (1680-1691 cm^{-1}) for all bindone derivatives that also exist in the triketo form: bromobindone, dibromobindone, bromonitrobindone, dinitrobindone, methylbindone, bromomethylbindone, and nitromethylbindone. The second frequency varies considerably depending on the character of the substituent introduced into the α-position in the indanone ring. This frequency increases from 1716 cm^{-1} in bindone to 1719 cm^{-1} in bromobindone and 1732 cm^{-1} in dibromobindone. An especially strong increase in the frequency of the C=O group is caused by the nitro group (1740 cm^{-1} for nitromethylbindone, 1749 cm^{-1} for nitrobromobindone, and 1752 cm^{-1} for dinitrobindone). An increase in the frequency of C=O vibrations by bromine and the nitro group is also characteristic of other indanone-1 derivatives (11, 12).

It should be assumed that the frequency 1716 cm^{-1} in the spectrum of bindone includes, in addition to the C=O vibration of the indanone ring, also the second (resonance) frequency of C=O of the indandione ring, which is likewise strongly lowered in comparison with the resonance frequency of the carbonyl of the indandione ring (9). In a molecule where the double bond is hydrogenated, or where a nitro group has been introduced into the α-position, this frequency appears in pure form (1744 cm^{-1} in indanonyl-indandione, 1730 cm^{-1} in nitromethyl- and dinitrobromobindone, 1723 cm^{-1}

Table 2

Dependence of the half-wave potential $E_{1/2}$ (in volts) on pH

Compound	Equation of the first wave (entire pH interval)	Equation of the second wave	Equation of the third wave	Equation of the fourth wave (alkaline medium)
Bindone	–	$-0.61 - 0.074\,\text{pH}$	$-0.91 - 0.048\,\text{pH}$	-1.45
Bromonitrobindone	$-0.26 - 0.078\,\text{pH}$	$-0.54 - 0.080\,\text{pH}$	$-0.93 - 0.036\,\text{pH}$	-1.45
Dinitrobindone	$-0.05 - 0.098\,\text{pH}$	$-0.46 - 0.094\,\text{pH}$	$-0.72 - 0.060\,\text{pH}$	-1.45
2-Bromo-2-nitroindandione-1,3	$-0.29 - 0.085\,\text{pH}$	$-0.54 - 0.078\,\text{pH}$	$-0.94 - 0.035\,\text{pH}$	-1.40
Indandione-1,3	–	$-0.58 - 0.050\,\text{pH}$	$-0.87 - 0.014\,\text{pH}$	-1.40

in bromonitrobindone), owing to a considerable shift of the indanone frequency.

In nitromethylbindone the frequency 1557 cm^{-1} corresponds to the asymmetric vibration of the nitro group, as in anhydrous 2-nitroindandione-1,3 (1560 cm^{-1}) (13). The introduction of bromine or of a second nitro group into the geminal position considerably increases the frequency of the nitro group, up to 1601 cm^{-1} for dinitrobindone. In the IR spectrum of the monoxime of bindone there are frequencies of 1690 and 1724 cm^{-1}, which may be assigned to vibrations of the indandione ring; consequently, oximation takes place in the indanone ring. In addition to the above-mentioned frequencies, in all the compounds mentioned, in the range 1550–1610 cm^{-1}, there is a series of frequencies associated with vibrations of the conjugated aromatic system, overlapping the vibration of the double bond in bindone and disappearing in the absence of continuous conjugation (in indanoylindandione, at 1608 cm^{-1}, only the vibration of the benzene ring appears).

The character of the IR and UV spectra recorded by us for isobindone—a compound to which structure II has been assigned—cannot be completely interpreted on the basis of the formula mentioned, and the question of the structure of isobindone remains open for the present.

The IR spectrum of the potassium salt of bindone indicates a significant difference between the structure of the bindone anion and the undissociated triketo form. In the anion the frequencies are strongly shifted and, in addition, a series of new frequencies appears in the region of shifted vibrations of the double bond (1480–1600 cm^{-1}), which individually cannot be assigned, indicating the existence of a mesomeric anion (IV).

(structural formula IV)

(IV)

It is interesting to note the similarity of the IR spectra of the potassium salts of bindone and isobindone, as well as the possibility of mutual conversion of these salts, established chemically ([8,14]). In this connection it is appropriate to raise the question of the identity of the structures of the anions of bindone and isobindone.

It should be noted that the triketo form tends to pass, in polar solvents (water, alcohol), into the anionic form, characterized by absorp-

absorption at ~5300 Å. Freshly prepared alcoholic solutions of bindone, bromobindone, and bromonitrobindone have a yellow color, which on prolonged standing or on boiling gradually changes to an intense red.

The polarogram of bindone shows waves characteristic of the polarogram of indandione-1,3, caused by reduction of the carbonyl groups; in an acidic medium $E_{1/2}$ depends on pH, and the reduction process here occurs in two stages ($E_{1/2} = -0.98$ V and -1.15 V at pH 5), presumably with intermediate formation of a free-radical carbinol[15]. In an alkaline medium $E_{1/2}$ becomes independent of pH ($E_{1/2} = -1.45$ V), and at pH > 10 the clearest waves are obtained, suitable for the quantitative determination of bindone, which opens prospects for the development and application of polarographic and amperometric methods when using bindone as an analytical reagent. The polarogram of bromonitrobindone is analogous to the polarogram of 2-bromo-2-nitroindandione-1,3: the wave at more positive potentials ($E_{1/2} = -0.65$ V at pH 5) is due to reduction of the nitro group, while the subsequent waves ($E_{1/2} = -0.94$ V and -1.11 V at pH 5) are associated with reduction of the carbinols. The nitro group in bromonitrobindone is reduced at the same potential as in 2-bromo-2-nitroindandione-1,3.

The polarographic reduction of dinitrobindone is the second example of polarographic reduction of two geminal nitro groups; in the present case the process occurs at more positive potentials than the reduction of 2,2-dinitropropane[16], and is characterized by a considerable dependence of $E_{1/2}$ on pH, which is not observed for 2,2-dinitropropane; at pH > 8 the height of the polarographic wave decreases. The subsequent waves at more negative potentials are associated with reduction of the carbinols.

Thus, the character of the polarographic reduction of bindone derivatives is determined to a much greater extent by the presence of the indandione ring in the molecule than by the introduction of individual active substituents.

It follows from the foregoing that bindone in the solid state corresponds to formula (I), proposed by Wislicenus, while upon dissociation of the molecule an anion of structure (IV) is formed.

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