

## On Infrared Absorption Spectra of 2-Nitroindandione Derivatives

by

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In an earlier paper [1], when determining the reaction products of 2-nitroindandione-1,3 with benzhydrol derivatives, by means of the infrared absorption spectrum the present authors found these compounds to have — in the range of frequencies typical for the C=O group — three absorption bands differing in intensity, whenever the diphenylmethyl (benzhydryl) rest lay in position 2.

This phenomenon has not, so far, been described in the literature, perhaps, because the infrared absorption spectra of 2-nitroindandione-1,3 and its derivatives have not been examined.

Data concerning investigations of the infrared spectrum of indandione-1,3, itself are also scanty [2]—[10]. In many cases, the interpretation of the spectra and the classification of the examined compound among these  $\beta$ -diketones does not take into account the specificity of structure, nor the influence of substituents on the localization of the absorption bands and is based solely on casual agreement with manual data [3]. We have treated the problem of indandione-1,3 derivatives absorption spectra more extensively and it will be the subject of our subsequent papers.

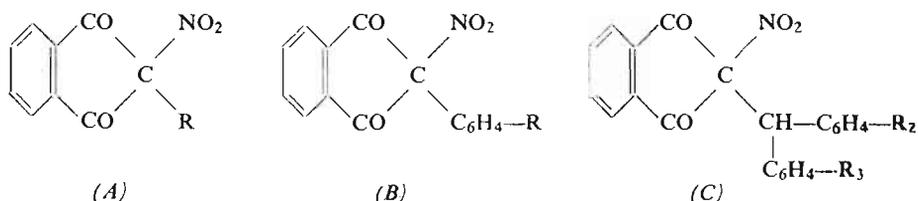
A more detailed examination of indandione-1,3 and its derivatives seemed the more interesting, because a series of biologically active compounds was found in this group, such as anticoagulants [12]—[14], zoocides [15], diuretics [16], pyrethrum synergists [17], [18] and so on. The knowledge of the infrared absorption spectra of these compounds may enable us to elaborate methods of their identification and quantitative determination, e.g. in systemic fluids etc.

The problem of characterizing the spectra of 2-nitroindandione-1,3 and its derivatives is, moreover, closely connected with our studies of infrared spectra of nitroparaffins. In fact, the 2-nitroindandione-1,3 derivatives should be classified as nitroparaffin derivatives. Moreover, the phenomenon of appearance of three bands characteristic of the C=O group in  $\beta$ -diketones and their shift to larger wavelengths attracted attention. It gave rise to some doubts as to the structure of the reaction products of 2-nitroindandione-1,3 with benzhydrol and its derivatives.

Vanag [19] considered the possibility of formation of a  $\gamma$ -diketone system as a result of extending the indandione ring. The possibility of obtaining a lactam form [11] ought to be taken into account, too.

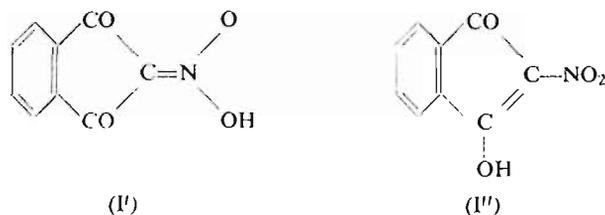
The present paper is an attempt to explain this phenomenon, since it seemed that the appearance of these three bands may as well be caused by the influence of the nitro group as by the diphenylmethyl rest in position 2. Both these substituents may influence the frequencies of the two carbonyl groups fixed in position *trans* [10].

A number of 2-nitroindandione-1,3 derivatives was investigated, the structure of which may be represented by the general formulae (A), (B) and (C):



In these compounds in position 2 — besides the nitro group — a substituent was always present which in one case only (A; R=H) made possible the tautomeric transformation of the ketone or nitro group.

According to Vanag's investigations [19], 2-nitroindandione-1,3 (I) has the character of a strong acid. With organic as well as with inorganic bases it forms a number of salts. The problem is open, which of the two possible tautomers is responsible for this phenomenon.



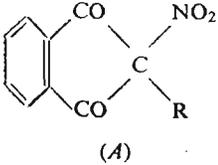
Results of examination of the spectra of 26 derivatives of (A), (B) and (C) type are listed in Tables I and II.

In these Tables only bands common to the compounds (I)—(XXVI) in the range 1800—750  $\text{cm}^{-1}$  are given. The spectra were determined with the use of an automatic recording double beam Hilger spectrophotometer H-800 with a 60° sodium chloride prism. The apparatus was calibrated in reference to a standard polystyrene membrane in several spectrum ranges, the determination error did not exceed  $\pm 3 \text{ cm}^{-1}$ . The substances were investigated in the form of a paraffin oil mull; while in the oil's absorption ranges, bromotrichloromethane was used as suspending agent.

All substances were prepared according to Vanag's methods [19] or their preparation followed the methods described in our earlier papers [1], [20].

TABLE I

Comparison of infrared absorption spectra of 2-nitroindandione-1,3 derivatives with general structure (A)

No. R	I	II	III	
	H	Cl	Br	
 (A)	1722 w 1684 sh 1650 vs 1641 vs 1590 s	1783 s  1750 s  1721 vs  1586 s 1572 vs	1764 s  1736 s 1717 vs  1642 vw 1581 sh 1572 vs	paraffin oil mull
	1470  1401  1366	1467   1362  (1342)*  1331  1293	1462 1424  1391  1356 1342 (1349)*  1321 1288	BrCCl <sub>3</sub> mull
	1269 s  1146 vs 1036 s	1240 s	1239 s	paraffin oil mull

\*) In CCl<sub>4</sub> solution; concentration of the substance investigated — 0.01 per cent.

Legend as in Table II

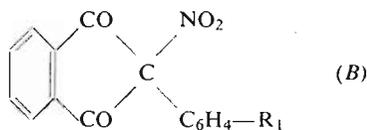
## Discussion

Examination of the absorption spectrum of the fundamental compound, i.e., 2-nitroindandione-1,3 (I) proved that it does not contain the band characteristic for asymmetric and symmetric stretching vibrations of the aliphatically linked nitro group. On the contrary, it displays a very intense band with a weakly marked maximum split into two peaks: 1641 and 1650 cm<sup>-1</sup>; its structure is complex, as may be inferred from the gentle bend at the frequency of 1684 cm<sup>-1</sup>.

This band in the spectrum should be ascribed to the frequencies of the C=N stretching band in the system of indandione-1,3-nitronium-2 acid (I). This view is supported by literature data (although rather scarce) concerning the spectra of nitronium acids, which are very difficult to investigate, because of their known instability. Our assertion is, moreover, corroborated by the fact that *aci*-9-nitrofluorene, a very stable compound [21] known only in the form of nitronium acid

TABLE II

Comparison of infrared absorption spectra of 2-nitroindandione-1,3 derivatives with structure (B)

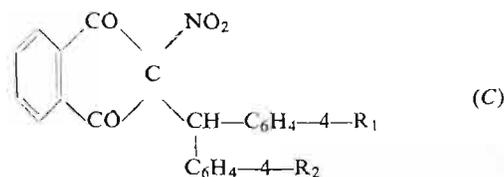


No.	IV	V	VI	VII	VIII	IX	X	XI	XII	
R <sub>1</sub>	H	3-NO <sub>2</sub>	4-NO <sub>2</sub>	4-CH <sub>3</sub>	4-F	4-Cl	4-Br	4-J	4-CH <sub>3</sub> O	
	1780 w 1750 s 1715 vs	1782 w 1750 s 1712 vs	1788 w 1750 s 1716 vs 1693 sh	1783 w 1750 m 1717 vs	1774 w 1750 m 1717 vs	1783 w 1752 m 1717 vs	1778 w 1752 m 1717 vs	1783 w 1752 m 1719 vs	1780 w 1746 s 1715 vs	paraf- fin oil mull
	1605 1583 s 1543 vs	1581 s 1557 vs 1528 vs	1609 m 1585 s 1552 vs 1518 vs	1646 vw 1609 vw 1590 m 1550 vs 1509 vw	1609 1580 m 1552 vs 1509 s	1649 vw 1590 m 1547 vs 1490 m	1647 vw 1609 w 1585 m 1548 vs 1481 m	1647 vw 1614 vw 1578 m 1546 vs	1604 s 1585 s 1538 vs 1505 s	
	1495	1481 1462	1467	1467		1467	1481	1478	1467 1422	BrCCl <sub>3</sub> mull
	1448	1432	1410	1405 1373	1410	1403	1398	1393	1362 1342	
	1359 1342	1350	1350	1350	1358 1339	1357	1354 1340	1354 1340	1326	
	1326	1297	1331	1331	1320	1328	1321	1321	1314	
	1262	1260	1287 1259		1277				1260 vs	
	1259 vs	1259 vs	1259 vs	1254 s	1240 s 1224 s	1252 s	1255 s	1252 s	1254 vs	paraf- fin oil mull
	1222 s	1222 s	1215 s 804 s	1212 m	807 s	1217 m	1217 m		1217 s 804 s	
	809 s	802 s	785 s	785 s	774	797 s	793 s	792 m		
	777 s	774 m	775 m	765 m		769 m	769 m	769 m	769 m	

Legend: w — weak, s — strong, vs — very strong, m — medium, sh — shoulder

TABLE III

Comparison of infrared absorption spectra of 2-nitroindandione-1,3 derivatives with the structure (C)

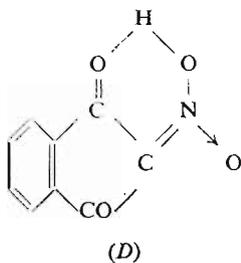


No.	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV	XXV	XXVI		
R <sub>1</sub> ; R <sub>2</sub>	H; H	F; F	Cl; Cl	Br; Br	J; J	CH <sub>3</sub> O; CH <sub>3</sub> O	C <sub>2</sub> H <sub>5</sub> O; C <sub>2</sub> H <sub>5</sub> O	F; Cl	F; Br	F; CH <sub>3</sub>	F; CH <sub>3</sub> O	F; C <sub>2</sub> H <sub>5</sub> O	F; CH <sub>3</sub> S	F; H		
	1785 w 1754 s 1719 vs 1645	1781 w 1752 s 1716 vs 1601	1791 w 1752 s 1712 vs 1618	1783 w 1750 s 1712 vs 1626	1788 w 1752 s 1716 vs 1647	1783 w 1746 s 1712 vs 1641	1785 w 1748 s 1712 vs 1604	1783 w 1752 s 1717 vs 1651	1785 w 1752 s 1717 vs 1603	1783 w 1750 s 1717 vs 1604	1788 w 1750 s 1717 vs 1604	1788 w 1750 s 1712 vs 1609	1783 w 1752 s 1717 vs 1590 m	1783 w 1752 s 1712 vs 1590 m	1783 w 1752 s 1712 vs 1590 m	paraffin oil mull
	1455	1443 1411	1410	1405	1400	1461 1453	1467 1439 1414 1390	1494	1486	1418	1415	1462 1439	1465 1439	1481 1429	1449	BrCCl <sub>3</sub> mull
	1359 1342 1326 1264	1353 1345 1323	1362 1340 1326	1358 1338 1321	1360 1340 1321	1364 1342 1325	1354 1342 1321 1302	1412 1362 1337 1321	1410 1361 1342 1326	1418 1364 1345 1325	1415 1363 1339 1321	1410 1355 1339 1319	1396 1354 1335 1321	1397 1335 1321		
	1259 vs 1236 1033	1257 vs 1231 vs 1039 1019	1259 s 1238 s 1019	1257 s 1231 1010	1251 s 1236 s 1024	1250 vs 1033 vs	1254 vs 1236 s 1024	1257 s 1240 s	1257 s 1236 s	1260 s 1236 s	1264 vs 1245 vs 1038 vs	1250 vs	1257 vs 1238 s	1259 s 1231 vs 1028		paraffin oil mull
	1000 972 936 892 807 w	967 924 896 827 s 815 s	970 927 897 826 m 807 s	972 924 897 804 m	967 919 891 821 804 s	1005 919 891 826 vs 812 vs	1007 972 922 892 821 812	1000 967 927 895 826 m 807 m	1000 967 927 892 821 m 804 m	1000 967 934 894 821 m 802 sh	1003 967 922 896 812 s	1002 967 919 892 812 s	1000 962 924 892 807 m	1000 972 919 896 812 s		

Legend as in Table II

gives a C=N band at  $1652\text{ cm}^{-1}$  which is shifted to  $1622\text{ cm}^{-1}$  when the compound is deuterized (or in chloroform solution [24]). The spectra of acyl derivatives of nitronium acids [23], [24], i.e., of mixed anhydrides exhibit shifts of this band towards  $1610\text{--}1642\text{ cm}^{-1}$  values and its position obviously depends on the structure of the nitronium acid, the acylating agent remaining unchanged. The C=N band of the benzaldoxime N-oxide [25] (which should be regarded as a mixed anhydride of phenyl *aci*-phenylnitromethane and benzaldoxime) is of medium intensity and lies at  $1689\text{ cm}^{-1}$ . The same band of *aci*-2-nitro-3-(*p*-anisyl)-norbornane [27] lies at  $1629\text{ cm}^{-1}$  (for  $\text{CHCl}_3$  solution). Similarly, in the case of *aci*-tetranitroalkanes spectra [26], it was found that the frequencies characteristic of the C=N bond of the corresponding nitronium acid appear at  $1667\text{ cm}^{-1}$ .

Equally, in the 2-nitroindandione-1,3 (I) spectrum an absorption band at  $3457\text{ cm}^{-1}$  (paraffin oil mull) was found which shifted towards  $3422\text{ cm}^{-1}$  (suspension in  $\text{BrCCl}_3$ ). It seems that this band may be ascribed to the frequencies of the OH group with an intramolecular hydrogen bond and with one of the carbonyl groups (D) participating in its formation:



It is worth noting that, in the investigations on nitronium acids carried out so far, some authors [11], [21], [23]—[27] stress the absence of bands characteristic of the OH group in the spectra investigated by them, while others pass this matter under silence. Only Zimmerman and Nevins [22] observed in the *aci*-1-nitro-2-phenylcyclohexane spectrum a wide band of the OH group in the  $3448\text{--}2632\text{ cm}^{-1}$  range.

Besides the bands already mentioned in the spectrum of compound (I), another band was observed of the frequency  $1722\text{ cm}^{-1}$  and weak intensity — which may be ascribed to the vibrations of the C=O group — and a strong band at  $1590\text{ cm}^{-1}$ . Investigation of other 2-nitroindandione-1,3 derivatives lead to the conclusion that the band in the  $1590\text{--}1578\text{ cm}^{-1}$  range is characteristic for the compounds (I)—(XXVI). Its intensity depends — to a certain degree — on the substituent in position 2. Its presence is due to the vibrations stretching the C—C bonds of the benzene ring.

Bands similar in intensity were observed by Gonzalez-Sanchez [28] in benzenedi- and -polycarboxylic acids, particularly with substituents in position *ortho*. From the foregoing considerations as well as from spectrum data we may infer, that 2-nitroindandione-1,3 (I) presents an interesting case of stabilization of the *aci*

form (corresponding nitronium acid). This, maybe, is due to the intramolecular hydrogen bond suggested in formula (D).

If a chlorine (II) or bromine (III) atom is introduced in position 2 into the 2-nitroindandione-1,3 system, we observe first of all the disappearance of the OH group band. In the C=O group absorption range three bands appear differing in intensity (II; 1783, 1750 and 1721  $\text{cm}^{-1}$ ) and (III; 1764, 1736 and 1717  $\text{cm}^{-1}$ ), whereas the bands characteristic of the stretching vibrations of the C—C bonds in the benzene ring appear at 1586 and 1581  $\text{cm}^{-1}$ . Simultaneously, we may observe at 1572 and 1571  $\text{cm}^{-1}$  very strong bands characteristic of asymmetric vibrations of the nitro group. If we compare the frequencies of this band in compounds (II) and (III) with the frequencies of asymmetric vibrations of the NO<sub>2</sub> group in the derivatives (IV)—(XXVI), it is clearly seen that they are shifted towards shorter waves (shift about  $\Delta$  15—34  $\text{cm}^{-1}$ ). It is due to the influence of the halogen atom on the aliphatic nitro group bands. This phenomenon was already observed by other authors [3].

A similar effect — the appearance of three absorption bands in the C=O group absorption range — is obtained not only by the substitution of hydrogen in position 2 by a halogen but equally by introducing an aryl rest (B; (IV)—(XII)) or diarylmethyl (C; (XIII)—(XXVI)). The first of these bands in the 1791—1774  $\text{cm}^{-1}$  range is weak, whereas the two following ones, in the 1754—1746  $\text{cm}^{-1}$  and 1712—1719  $\text{cm}^{-1}$  regions, are strong, resp. very strong. The two latter bands are characteristic of a system of *trans*-fixed  $\beta$ -diketones. As shown by our investigations, they lie for indandione-1,3 at frequencies 1741 and 1703  $\text{cm}^{-1}$  (in the literature they are reported to appear at 1750—1710  $\text{cm}^{-1}$  [5], [30]) and for the case of 2-benzylidencindandione-1,3 they are shifted to 1737 and 1696  $\text{cm}^{-1}$  [30]. Cyclopentendione-3,5 has, similarly, two absorption bands [29], [30], in the 1748 and 1712  $\text{cm}^{-1}$  ranges.

In our further investigations we succeeded in elucidating the cause of the appearance of a weak band (in the 1791—1774  $\text{cm}^{-1}$  range) in the region of the C=O group vibrations. It was found that its appearance is due to the presence of the NO<sub>2</sub> group as a substituent in position 2 of indandione-1,3. More detailed data concerning this phenomenon will be the subject of a separate paper.

The assertion that 2-nitroindandione-1,3 and its derivatives (IV)—(XXVI) belong to the nitroparaffin class is supported by the characteristic frequency of asymmetric stretching vibrations of the NO<sub>2</sub> group in the 1538—1557  $\text{cm}^{-1}$  range. In the spectra of compounds (V) and (VI) — which contained in position 2 3'-nitro- and 4'-nitrophenyl rests as substituents — very intensive bands of asymmetric vibrations of the aromatically linked nitro group were found. These bands appear in the 1528—1518  $\text{cm}^{-1}$  range.

The identification of the bands of symmetric stretching vibrations of the aliphatic nitro group in the compounds investigated ((II)—(XXVI)) was not easy on account of the suspension technique applied. Moreover, when bromotrichloromethane as suspending agent was used, its evaporation occurred sometimes during measurements, changing the intensity relations of the particular bands. In the case

of compounds (II) and (III), this problem was solved by examining a 0.01 per cent solution in  $\text{CCl}_4$ . Thus, we were able to ascribe the bands 1342 and 1349  $\text{cm}^{-1}$  to the symmetric vibrations of the aliphatic  $\text{NO}_2$  group of the investigated products. In compounds of structure (B) the same vibrations should be ascribed to the bands in the 1350—1362  $\text{cm}^{-1}$  range. For the compounds of (C) type these bands are also present in the 1353—1364  $\text{cm}^{-1}$  region. It should be noted that they were not identified by investigation in highly diluted solutions.

All other bands with different intensity in the 1625—1450  $\text{cm}^{-1}$  range are associated with the vibrations of the C—C bonds of the benzene ring. Also bands below 1250  $\text{cm}^{-1}$  represent deformation vibrations of the C—H bonds, out- and in-plane vibrations, benzene ring skeletal vibrations and so on. They are all very difficult to identify. In Tables I and II only those bands common to all compounds are given; their localization is given with an error not exceeding  $\pm 10 \text{ cm}^{-1}$ .

It should be noted that in the range of what is called "fingerprint" the spectra of benzhydryl 2-nitroindandione-1,3 derivatives, i.e. of compounds of type (C) are far more complex and contain more bands than those of 2-aryl-2-indandiones-1,3 of the structure (B).

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