Dipole moments of the carbonyl groups in cyclic β-diketones from IR spectroscopy data

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The α_{CO} angles between the carbonyl groups and the dipole moments of a number of 2-arylindan-1,3-diones were determined from the data of IR spectroscopy. The effects of substituents on α_{CO} depending on their positions and inductive factors were found. It was established that the interaction between the vibrations of the carbonyl groups depends on both the α_{CO} angle or the $\Sigma\mu_{CO}$ dipole moment and the coplanar arrangement of these groups.

Key words: IR spectroscopy; dipole moments; coplanar arrangement; carbonyl groups; 2-arylindan-1,3-diones.

The mechanical interaction of two independent vibrations of carbonyl groups in cyclic β-diketones produces[1] a doublet of absorption bands in the stretching region (1750—1680 cm^{-1}) in which the asymmetric vibration is characterized by a higher intensity. The stronger the interaction between the vibrations, the greater the difference between the frequencies of the components of the doublet (ν(CO) increases).[2] The two carbonyl groups must be coplanar in order to interact.[3] The vibrations of the carbonyl groups that result in an increase in the dipole moment (asymmetric vibrations) make the greatest contribution to the absorption bands.

An equation has been suggested[4] for determining the α_{CO} angle between the interacting carbonyl groups in molecules having C_2 symmetry with respect to the carbon atom

$$A_{as}/A_s = tg^2\ 1/2\ \alpha_{CO}, \qquad (1)$$

where A_{as} is the integral intensity of the bands of the asymmetric vibration and A_s is the integral intensity of the bands of the symmetric vibration. The values for the α_{CO} angles calculated from this formula for cyclic imides and anhydrides of dicarboxylic acids are in good agreement with X-ray diffraction data.[5] The only cyclic β-diketone to which this formula has been applied[5] is 2-benzylidene-1,3-indandione (α_{CO} = 132°). For 2-aryl- and 2-arylidene-1,3-indandiones, the integral intensities of the absorption bands corresponding to the carbonyl groups have been represented[6] only as the sum $\Sigma A_{CO} = A_{as} + A_s$.

The purpose of the present work is (1) to determine the α_{CO} angles between the axes of the carbonyl groups for a series of cyclic β-diketones; (2) to compare the resulting values of α_{CO} with the α_{CO} angles in compounds for which X-ray structural studies have been carried out; (3) to follow the variation in the α_{CO} angles as a function of the positions of substituents and as a function of the inductive and steric factors; and (4) to consider the dependence of Δν(CO) on the α_{CO} angle or on the dipole moments of the carbonyl groups, $\Sigma\mu_{CO}$.

Experimental

IR spectra were recorded on a Bruker IFS 45 spectrometer with a resolution of 2 cm^{-1} for pellets with KBr. Complex absorption bands due to the stretching vibrations of carbonyl groups were analyzed using the Bruker FIT program, which allows one to determine spectral characteristics of individual bands. The dipole moments of carbonyl groups arranged at the angle α_{CO} with respect to one another were determined by vector addition of their moments, *i.e.*, from the formula:

$$\Sigma\mu^2_{CO} = \mu^2_{CO} + \mu^2_{CO'} + 2\mu_{CO}\mu_{CO}\cdot\cos\theta\cos\theta'\cos\alpha_{CO}. \qquad (2)$$

The θ angle is the angle between the direction of the group dipole moment and the bond.

For compounds with known group dipole moments of substituents, dipole moments of the indan fragments and of the whole molecules were calculated from the same formula (2). The β angle between the indan fragment and the benzene ring was taken to be 109°, since the C(2) carbon atom is sp^3-hybridized. The following group dipole moments were used:[7]

μ_{CO} = 2.96 D, θ = 146°; $\mu_{C_6H_5CH_3}$ = 0.37 D, θ = 0°;

$\mu_{C_6H_5N(CH_3)_2}$ = 1.58 D, θ = 30°; $\mu_{C_6H_5Br}$ = 1.57 D, θ = 180°;

μ_{CH_3Br} = 1.82 D, θ = 180°; $\mu_{C_6H_5Cl}$ = 1.59 D, θ = 180°.

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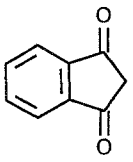

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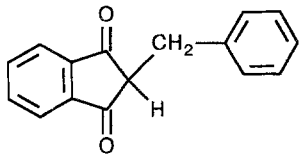

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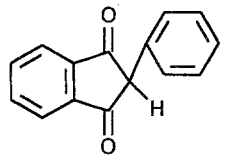

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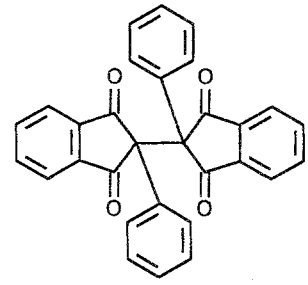

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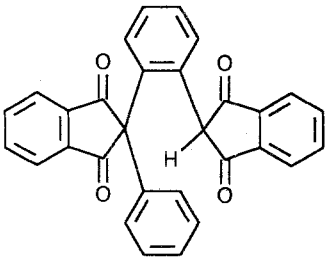

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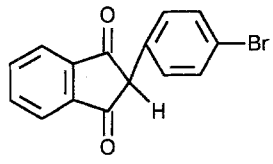

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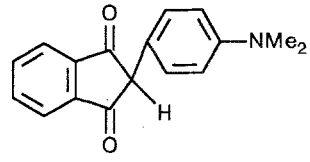

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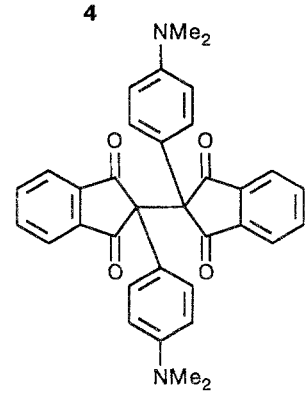

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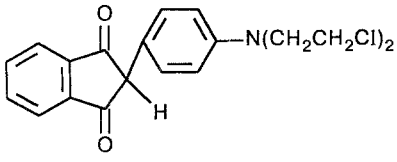

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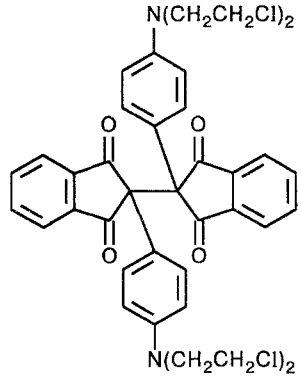

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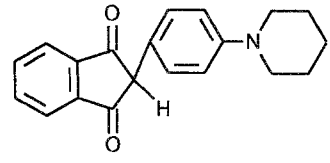

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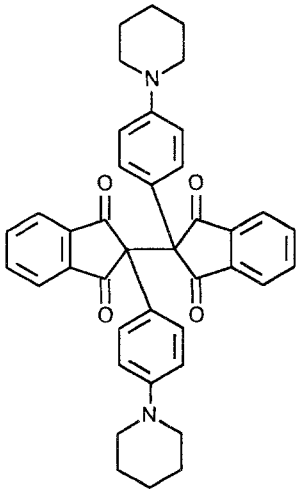

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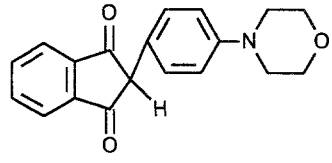

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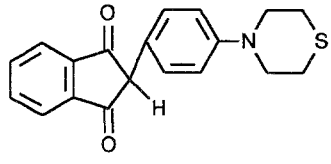

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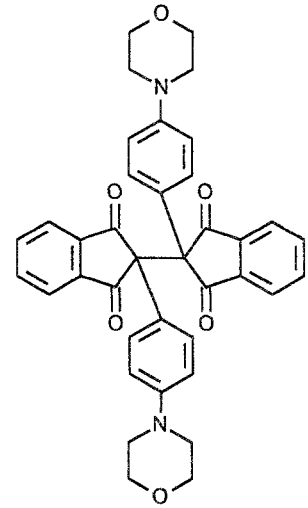

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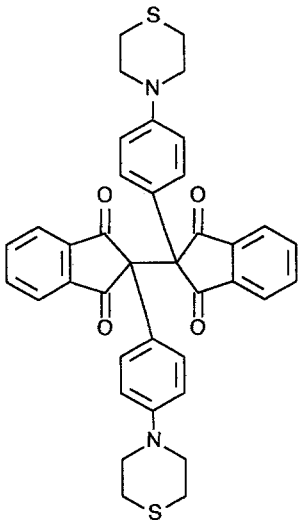

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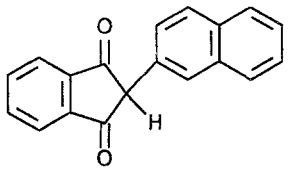

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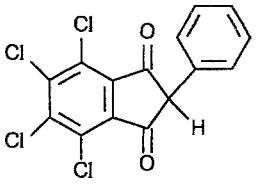

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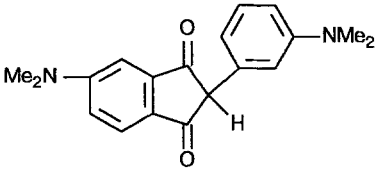

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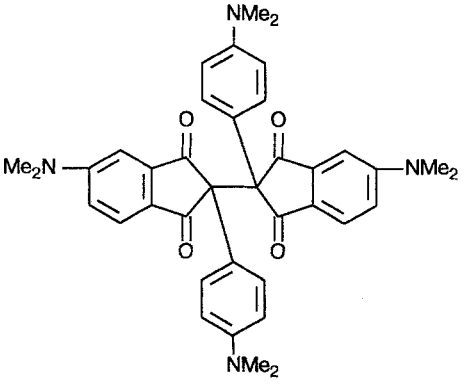

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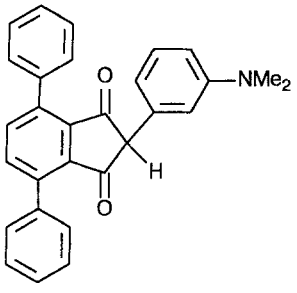

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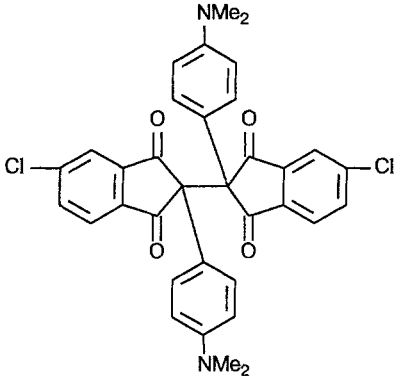

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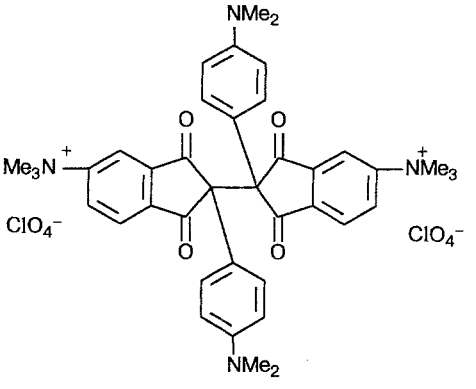

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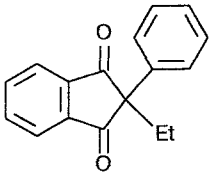

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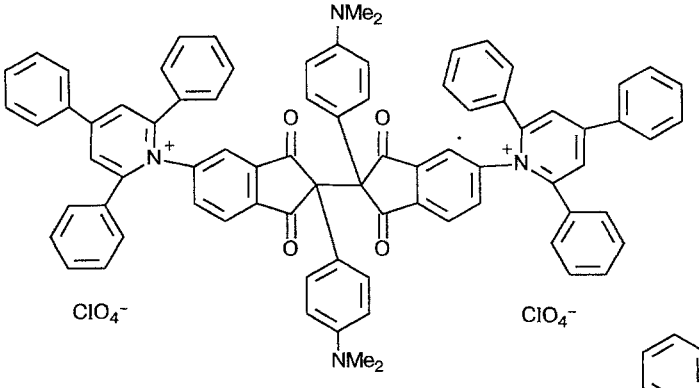

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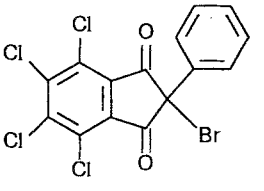

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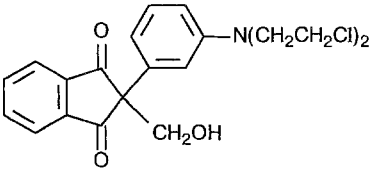

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Table 1. Characteristics of the carbonyl groups in cyclic β-diketones

Compound	ν(CO)/cm^{-1} as	ν(CO)/cm^{-1} s	Δν(CO)/cm^{-1}	A_{as}[a] (rel. units)	A_s[a] (rel. units)	A_{as}/A_s[b]	α_{CO}/deg	$\Sigma\mu_{CO}$/D
1[c]	1712	1751	39	—	—	—	148[d]	2.72[e]
2	1706	1746	40	6.68	1.13	5.91	135	3.03
3	1707	1746	39	29.97	5.42	5.53	134[f]	3.04
4	1711	1738	27	31.55	2.86	11.03	146	2.73
5	1712	1738	26	30.59	2.32	13.18	149	2.68
6	1708	1742	34	19.25	1.69	11.39	147[g]	2.72
7	1710	1744	34	19.76	3.86	5.12	132	3.08
8	1706	1736	30	48.03	4.90	9.79	145[h]	2.78
9	1708	1745	37	29.16	4.12	7.08	139	2.90
10	1707	1735	28	10.40	1.03	10.10	145	2.76
11	1712	1746	34	3.06	0.57	5.37	133	3.05
12	1709	1737	28	18.46	1.61	11.46	147	2.72
13	1708	1746	38	9.67	1.41	6.86	138	2.93
14	1708	1736	28	13.79	1.07	12.90	149	2.68
15	1712	1745	33	4.84	0.99	4.89	131	3.12
16	1708	1736	28	13.20	1.73	7.63	140	2.89
17	1707	1745	38	8.93	0.84	10.63	146[i]	2.74
18	1717	1748	31	31.36	5.04	6.22	136	2.98
19	1689	1727	38	15.52	3.78	4.11	128	3.19
20	1691	1728	37	14.16	3.90	3.63	125	3.27
21	1705	1739	34	14.37	3.00	4.79	131	3.10
22	1708	1740	32	28.44	6.21	4.58	130	3.13
23	1715	1749	34	5.84	1.10	5.31	133	3.05
24[j]	1698	1742	44	3.63	0.95	3.82	126	3.23
25	1715	1742	27	5.68	0.98	5.79	135	3.00
26	1720	1749	29	11.09	4.95	2.24	113	3.58
27	1706	1742	36	16.44	7.51	2.18	112	3.60

[a] The integral intensities of the carbonyl absorption groups are given.
[b] The ratio between the integral intensities of bands in the IR spectra.
[c] See Ref. 8. [d] See Ref. 9. [e] See Ref. 10. [f] *cf.* Ref. 11: α_{CO} = 136°. [g] *cf.* Ref. 12: α_{CO} = 148°. [h] *cf.* Ref. 13: α_{CO} = 148°. [i] *cf.* Ref. 14: α_{CO} = 147°. [j] See Ref. 15.

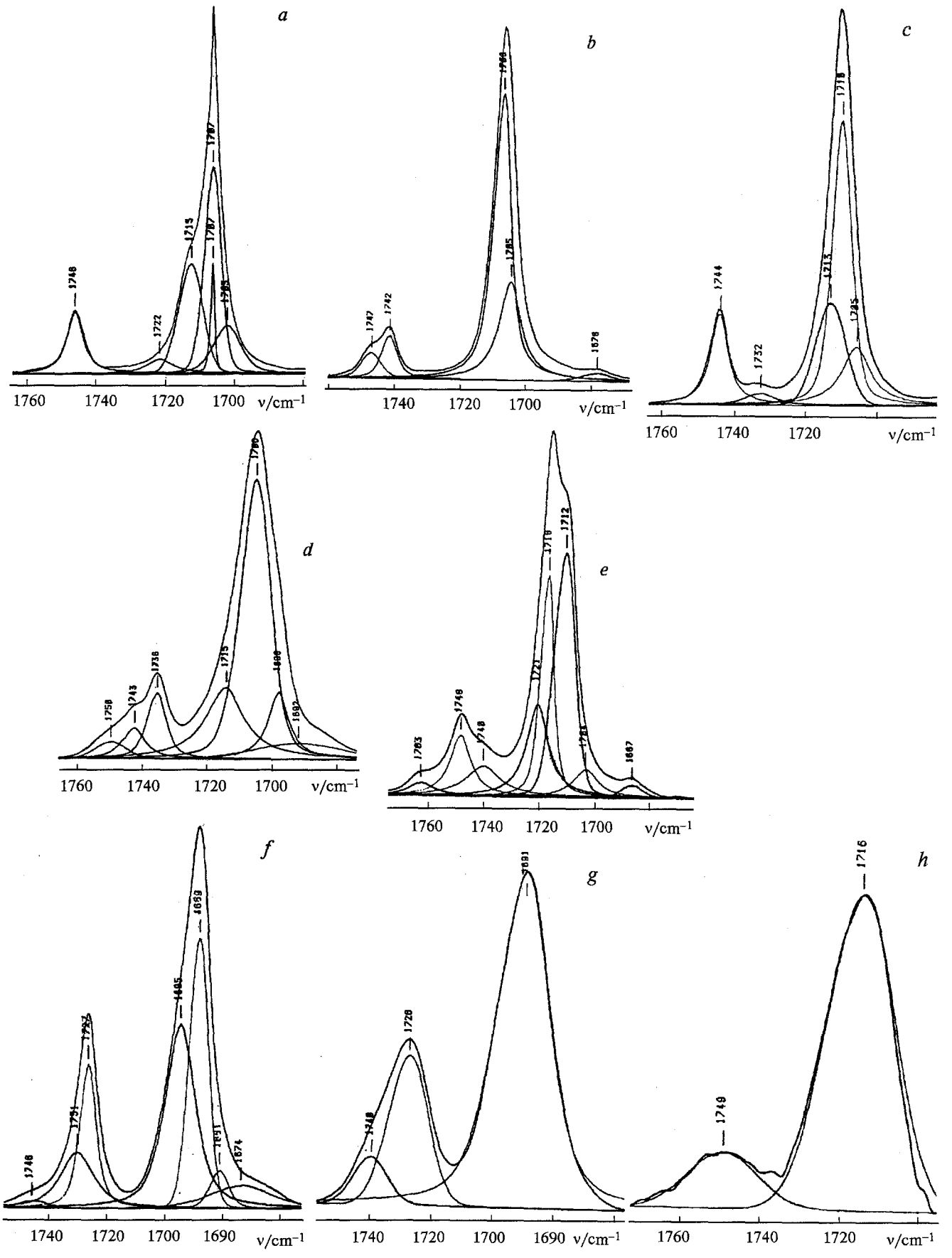
Results and Discussion

In the present work we have studied a series of cyclic β-diketones (**1**—**27**). The IR spectra of 2-arylindan-1,3-diones in the region of carbonyl stretching vibrations are presented in Fig. 1. The spectral characteristics of the absorption bands corresponding to the carbonyl stretching vibrations, the calculated angles α_{CO}, and the dipole moments $\Sigma\mu_{CO}$ are listed in Table 1.

It can be seen from the IR spectra obtained that each of the bands of the stretching vibrations of carbonyl groups (symmetrical and asymmetrical) has a complex structure. This is due either to the nonequivalence of the carbonyl groups in molecules with low symmetries or to distinctions in their environments in the solid phase. The dipole-dipole intermolecular interactions between the carbonyl groups result in distortions of the absorption bands observed. For highly shielded symmetrical indandiones (compound **23**), this type of interaction between the carbonyls is hampered, which is manifested in the spectrum as degeneration of the complex spectral bands into a doublet of symmetrical absorption bands (see Fig. 1, compound **23**).

Good agreement between the calculated α_{CO} values and the data of X-ray structural studies was achieved when the overall integral intensities of the bands corresponding to asymmetrical stretching vibrations and the integral intensity of the strongest absorption band corresponding to symmetrical stretching vibrations were used in Eq. (1). This method of calculation was used for all of the compounds. The α_{CO} angles found from Eq. (1) for compounds **3**, **6**, **8**, and **17** (see Table 1) are in good agreement with the X-ray diffraction data for these compounds.[11—14] The calculations of the α_{CO} angles and the dipole moments of carbonyl groups, $\Sigma\mu_{CO}$, allowed us to calculate the dipole moments of the indan fragments and of the whole molecules for some of the compounds (Table 2). The dipole moments obtained for the series of 2-arylindan-1,3-diones differ from each other; the values for compounds **18** and **19** differ from the other values most substantially.

The reliability of the calculations of the dipole moments is confirmed by the fact that the calculated and experimental values of μ for 2-phenylindan-1,3-dione (see Table 2, compound **3**) are in good agreement. The validity of the group dipole moments, the calculated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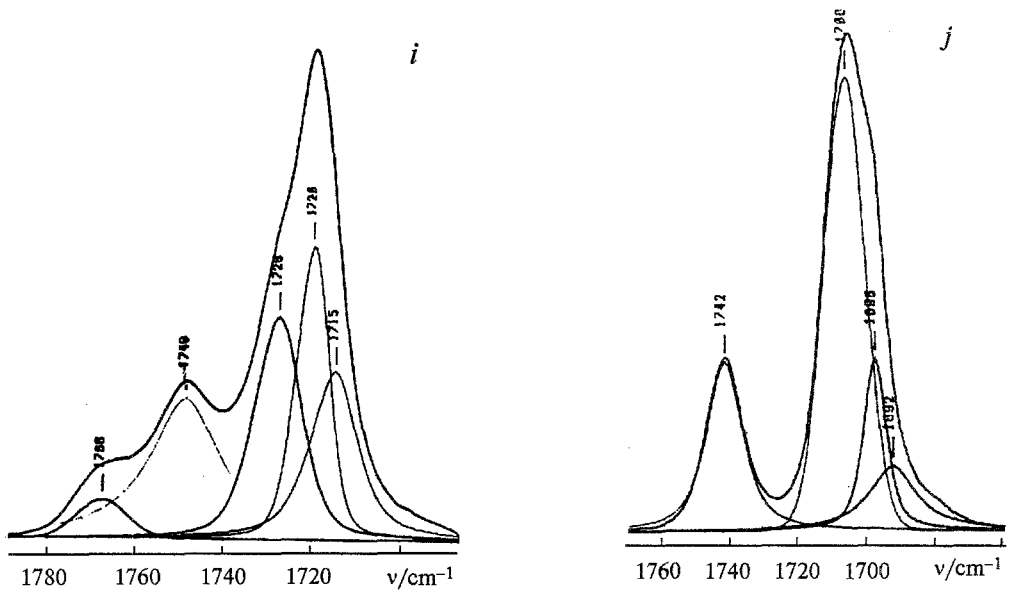

Fig. 1. The IR spectra of 2-arylindan-1,3-diones in the stretching region of carbonyl groups: **3** (*a*); **6** (*b*); **7** (*c*); **8** (*d*); **18** (*e*); **19** (*f*); **20** (*g*); **23** (*h*); **26** (*i*); **27** (*j*).

α_{CO} angles, the $\Sigma\mu_{CO}$ dipole moments, and the dipole moments of 2-arylindan-1,3-diones used in this work is also supported by the magnitude of the α_{CO} angle for compound **1** (see Table 1). The α_{CO} angle calculated from Eq. (2) taking into account the experimental[10] $\Sigma\mu_{CO}$ = 2.72 D, which is equal to 147°, is in good agreement with the α_{CO} = 148° determined by X-ray diffraction analysis.[9]

As the data of Table 1 indicate, for the series of cyclic β-diketones studied, no correlation between ν_s and ν_{as} is observed ($\nu_s \neq f(\nu_{as})$, Fig. 2). For the series of compounds under consideration the value of α_{CO} equal to 147±2° is the limiting value. Compounds with this limiting α_{CO} angle are mostly dimers (**4**, **5**, **8**, **10**, **12**, **14**), which contain no substituents in the indan fragment. The introduction of a benzene or toluene fragment into indandione-1,3 (compounds **2**, **3**) results in a decrease in the α_{CO} angle and, therefore, in an increase in the $\Sigma\mu_{CO}$ dipole moment (see Table 1).

Table 2. The calculated magnitudes of the dipole moments of 2-arylindan-1,3-diones

Compound	μ/D
3	2.94*
6	3.55
7	3.04
17	2.64
18	0.37
19	4.72
21	3.04
26	2.32

* Experimental value:[16] μ = 2.90 D.

It is of interest to follow the variation of the α_{CO} angle resulting from the introduction of substituents into the *para*-position of the benzene ring of 2-phenylindan-1,3-dione (**3**). The presence of electron-withdrawing Br (compound **6**) resulted in a substantial increase in α_{CO} and a decrease in $\Sigma\mu_{CO}$ (see Table 1). Electron-donating substituents, *viz.*, the NMe_2 group (compound **7**) and the piperidine residue (**11**), have virtually no effect on the α_{CO} angle or the $\Sigma\mu_{CO}$ dipole moment (see Table 1).

The effect of substituents in the indan fragment is the opposite of that of the substituents in the benzene ring. In fact, electron-withdrawing substituents have virtually no effect on the α_{CO} angle or the $\Sigma\mu_{CO}$ dipole moment (see Table 1, compounds **18**, **21**, **22**, **23**, **25**). The introduction of electron-donor substituents results in a substantial decrease in α_{CO} and in an increase in $\Sigma\mu_{CO}$ (see Table 1, compounds **19**, **20**).

However, electron-withdrawing substituents at the C(2) carbon atom, which is located in the immediate vicinity of the carbonyl groups, exert the greatest effect on the geometry of the indan fragment. In this case, the α_{CO} angle decreases to 112—113° and the dipole moment considerably increases: $\Sigma\mu_{CO}$ = 3.58 to 3.60 D (**26**, **27**).

Figure 3 shows the correlation between Δν(CO) and $\Sigma\mu_{CO}$, which allows the series of cyclic β-diketones under consideration to be divided into two groups. The first group consists of the compounds with the limiting α_{CO} angle, $\alpha_{CO} \geq 147\pm2°$, and, consequently, with the constant dipole moment, $\Sigma\mu_{CO}$ = 2.74±0.05 D (compounds **1**, **4**, **5**, **6**, **8**, **10**, **12**, **14**, and **17**). For these compounds, $\Delta\nu(CO) \neq f(\Sigma\mu_{CO})$ and changes in Δν(CO) are caused only by the coplanar arrangement of the carbonyl groups. This is confirmed by the X-ray structural

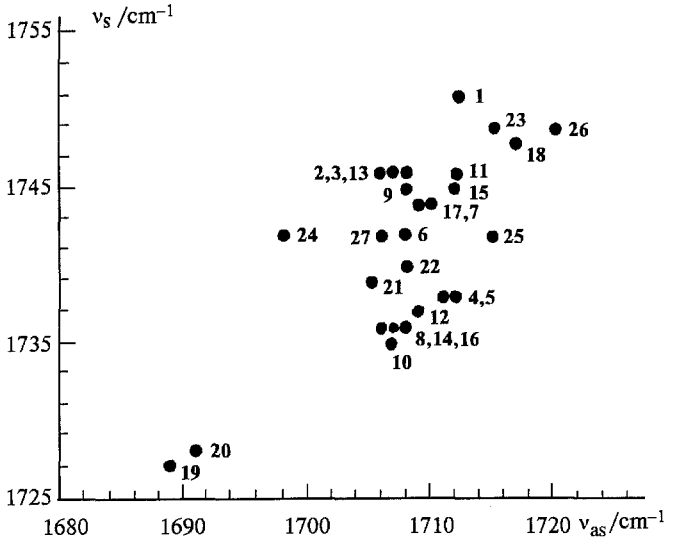

Fig. 2. The correlation between the symmetric (ν_s) and asymmetric (ν_{as}) stretching vibrations of the carbonyl groups in cyclic β-diketones. The numbers are the numbers used to identify the compounds.

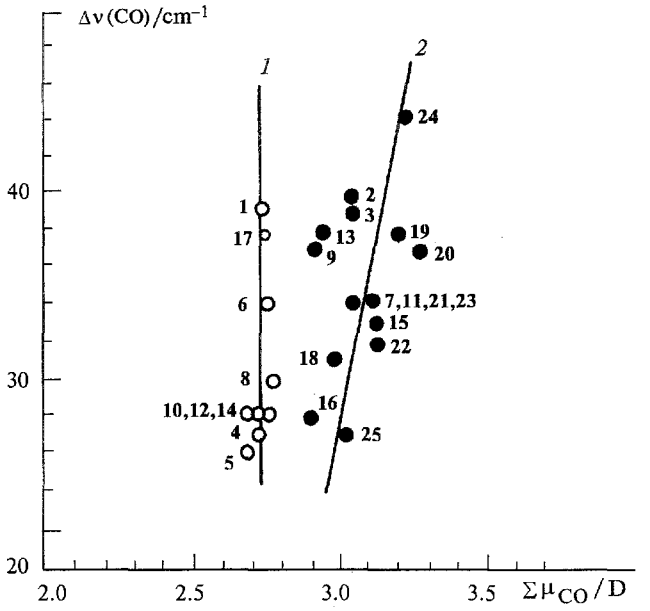

Fig. 3. The correlation between the interactions of the carbonyl groups and their dipole moments for compounds with $\alpha_{CO} \geq 147\pm2°$ (*1*) and $\alpha_{CO} \leq 140°$ (*2*).

study of compound **8**, which showed that the carbonyl groups in the indan fragment deviate[13] from the plane of the benzene ring by 3.8 and 0.8°. Compound **5**, which has the lowest Δν(CO) value (26 cm^{-1}) corresponds to a sterically strained isodimer of 2-phenylindan-1,3-dione.

All of the other compounds, for which $\alpha_{CO} \leq 140°$, belong to the second group. In this case, the variation of Δν(CO) is caused by the variation of the dipole moment, $\Sigma\mu_{CO}$, *i.e.*, Δν(CO) = f($\Sigma\mu_{CO}$). For these compounds, the smaller the angle between the carbonyl groups, the stronger the interaction between their vibrations (Δν(CO) increases). This condition is necessary, but is not sufficient. As for the first set of compounds, in this case, the coplanar arrangement of the carbonyl groups plays an important role. This can be readily seen by looking at compounds **19**, **20**, and **24**, for which the α_{CO} angles and the $\Sigma\mu_{CO}$ dipole moments are practically identical and the Δν(CO) values are different (see Fig. 3).

In the case of compounds **2**, **3**, **7**, **11**, **17**, **21**, **23**, as well as compounds **9**, **13**, **18**, **25**, for which the dipole moments $\Sigma\mu_{CO}$ are identical and Δν(CO) are different, the coplanar arrangement also makes a substantial contribution to the Δν(CO) value (see Fig. 3). This factor can also be easily seen in diketones **26**, **27**, whose $\Sigma\mu_{CO}$ are identical (see Table 1), and in which the difference between the Δν(CO) is accounted for by the effect of the Cl atoms on the coplanar arrangement of the carbonyl groups of the indan fragment, which is clearly demonstrated by the spectral characteristics of these compounds shown in Fig. 1.

Thus, the interaction between the vibrations of the carbonyl groups (Δν(CO)) depends on both the angle between them, α_{CO}, and on whether or not they are coplanar (a dual function).

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