# ON THE DEEP COLORATION OF THE ANIONIC FORMS OF CYCLOPENTENE-4-DIONES-1,3 AND INDANDIONES-1,3

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## Abstract

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# ON THE DEEP COLORATION OF THE ANIONIC FORMS OF CYCLOPENTENE-4-DIONES-1,3 AND INDANDIONES-1,3

We have shown previously ($^{1}$) that the anions of the cyclopentene-4-dione-1,3 and indandione-1,3 series are rather deeply colored and have a long-wavelength band at comparatively large wavelengths (440–552 mµ and higher ($^{2}$, $^{3}$)), although it is of low intensity. In this respect the compounds mentioned differ strongly from the anions of other $\beta$-diketones, for which the long-wavelength transition is usually intense and is located at a much shorter wavelength in the ultraviolet region, even in the presence of substituents with a strongly expressed $\pi$-electron system ($^{4}$). Since these differences are already observed in compounds without substituents in position 2, and such substituents have approximately the same effect on the spectra of all $\beta$-diketone anions, the cause of the deep coloration of the anions of cyclopentene-4-diones-1,3 and indandiones-1,3 must be sought in the presence of a five-membered cyclic structure with an attached double bond or benzene ring directly at positions 1 and 3 of the anionic 1,3-diketone system. The enolic forms and their simple ethers in these 1,3-diketones possess spectra and coloration rather close to those of the corresponding anionic forms, and their long-wavelength band is shifted only somewhat hypsochromically relative to that of the anions. The similarity of the absorption of the anions to that of the enols is in many cases also confirmed by calculations. In order to find confirmation of the hypothesis stated above concerning the causes of the deep coloration of the anions of cyclopentene-4-diones-1,3 and indandiones-1,3, we investigated the influence of ring closure through atoms in positions 1 and 3 on the energy and intensity of the long-wavelength $N \rightarrow V_1$ transition of the anions of 1,3-diketones.

Calculations predict a significant increase in the transition energy for the $N \rightarrow V_1$ transition without a noticeable change in its intensity upon formation of a direct bond between both carbonyl carbon atoms of the simplest anionic 1,3-diketone system (cf. I and II a, b). Consequently, ring formation by direct bonding of both carbon atoms in positions 1 and 3 without participation of a double bond should lead to a hypsochromic shift of the $N \rightarrow V_1$ band in comparison with the usual anion of 1,3-diketones, whose 1,3-overlap can be neglected. It is difficult to find confirmation of this, since the model substances, cyclopropanediones-1,3, are very strained compounds with a different type of bonding and valence state of the atoms than unstrained or slightly strained 1,3-diketones. Therefore, the observed increase in the hypsochromic shift of the $N \to V_1$ band, on passing from the anion of the cyclohexanedione-1,3 or cycloheptanedione-1,3 series ($^5$, $^{14}$) to its cyclopentanedione-1,3 analogue ($^6$), and further to cyclobutanedione-1,3 ($^7$, $^8$) and cyclopropanedione-1,3 ($^9$) anions, may arise not only at the expense of 1,3-overlap, but also because of the mentioned ring strain.

When the ring is formed by two double bonds, rather than one, as occurs in cyclopentene-4-diones-1,3, we obtain cycloheptadiene-4,6-dione-1,3, whose anion (V) should have a band even with a noticeable

Table 1

Calculated long-wavelength transition $N \to V_1$ of anions of certain $\beta$-diketones*

| Anion | $\Delta E_{N\to V_1}$ ($\beta_0$) | $D_{N\to V_1}$ (Å$^2$) | Anion | $\Delta E_{N\to V_1}$ ($\beta_0$) | $D_{N\to V_1}$ (Å$^2$) |
|---|---|---|---|---|---|
| [[structural formula of an acyclic $\beta$-diketone anion; axes $z$ upward and $y$ right are shown]] I | 1.3671 | 2.576 ($y$) | [[structural formula of a cyclic $\beta$-diketone anion]] V | 0.9301 | 1.071 ($y$) |
| [[structural formula of an acyclic $\beta$-diketone anion]] IIa | 1.5175 | 2.550 ($y$) | [[structural formula of an extended acyclic $\beta$-diketone anion]] VI | 1.3745 | 2.074 ($y$) |

| Anion | $\Delta E_{N\to V_1}$ $(\beta_0)$ | $D_{N\to V_1}$ $(\text{Å}^2)$ | Anion | $\Delta E_{N\to V_1}$ $(\beta_0)$ | $D_{N\to V_1}$ $(\text{Å}^2)$ |
|---|---|---|---|---|---|
| [[structural formula of an acyclic $\beta$-diketone anion]] IIb | 1.5175 | 2.550 $(y)$ | [[structural formula of a perinaphthindandione-1,3 anion]] VII | 1.0885 | 1.877 $(y)$ |
| [[structural formula of a cyclopentene-4-dione-1,3 anion]] III | 1.7570 | 2.486 $(y)$ | [[structural formula of a perinaphthindandione-1,3 anion]] VII | 0.9131 ** | 1.840 $(y)$ ** |
| [[structural formula of an indandione-1,3 anion]] IV | 0.7965 | 0.940 $(y)$ | [[structural formula of a dibenzoylmethane anion]] VIII | 1.0969<br>or<br>0.9320 ** | 1.804<br>or<br>1.909 $(y)$ ** |

* For the calculations the LCAO MO method in Hückel' s approximation was used ($^{13,14}$). The values of the Coulomb ($\alpha_P$) and resonance ($\beta_{rs}$) integrals were taken by us to be equal (approximation B ($^1$)). Table 1 gives only the calculated data for the $N \to V_1$ transition. The transition energy ($\Delta E_{N\to V_1}$) is expressed in terms of the standard resonance integral $\beta_0$, and the oscillator strength of the transition is given in $\text{Å}^2$. The polarization of the transition is indicated in parentheses. All molecules have $C_{2v}$ symmetry, and the long-wavelength $N \to V_1$ transition, belonging to the $A_1 \to B_2$ type, is symmetry-allowed.

** The calculations were carried out with different values of the Coulomb and resonance integrals (approximation A ($^1$)); therefore the numerical values of $\Delta E_{N\to V_1}$ and $D_{N\to V_1}$ cannot be compared with those for the other molecules, for which the values of the integrals differ (approximation B ($^1$)).

at shorter wavelengths than VI, which has one double bond in positions 1 and 3. It should be noted that the calculations we carried out do not predict any appreciable bathochromic displacement of the long-wavelength $N \to V_1$ band also for the anion of the cyclic $\beta$-diketone—perinaphthindione-1,3 (VII)—as compared with the anion of its acyclic analogue, dibenzoylmethane (VIII). These theoretical conclusions agree well with the available experimental data ($^{10-12}$). Consequently, the mere presence of a cyclic structure still does not ensure a large bathochromic shift of the long-wavelength $N \to V_1$ band of a $\beta$-diketone anion; rather, it is necessary that specifically the five-membered ring of the cyclopentene-4-dione-1,3 (III) or indandione-1,3 (IV) system be present, so that the usually intense $N \to V_1$ transition is sharply displaced from the ultraviolet region into the visible part of the spectrum, with a simultaneous loss of intensity. This distinctive and, in our view, important regularity holds not only among the anions and enols of the indandione-1,3 and cyclopentene-4-dione-1,3 series, but, apparently, also in the case of their nitrogen derivatives—imines, diimines, etc.—for which deep coloration has likewise been found, despite a comparatively small conjugated system ($^{13}$).

Linear condensation of cyclopentene-4-diones-1,3 with benzene rings, leading to the formation of indandiones-1,3 and 5,6-benzindandiones-1,3, gradually shifts the $N \to V_1$ band of their anionic form hypsochromically, but replacement of the hydrogen atoms at the double bond of cyclopentene-4-diones-1,3 by phenyl groups shifts the $N \to V_1$ band of the anion bathochromically ($^2$).

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*Note: Figure translations are in progress. See original paper for figures.*