Dyes and Pigments **18** (1992) 251–257

The Chromophore of Phenylazo-1,3-indandiones: The Azo Group or the Cyclopentadienyl Cation Fragment?

Fritz Dietz, Kerstin Rommel

Sektion Chemie, Universität Leipzig, Leipzig, Germany

&

Nikolai Tyutyulkov

Institute of Organic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria

(Received 21 August 1991; accepted 8 October 1991)

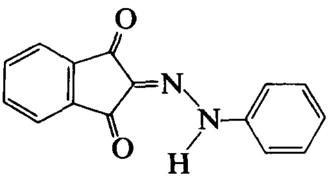
ABSTRACT

The structure and the absorption spectra of the tautomers of phenylazo-1,3-indandione were studied by quantum chemical methods (MNDO and PPP). In contrast to the interpretation of the experimental results, the enolazo tautomer is more stable and absorbs at significantly longer wavelength than the hydrazone form. The five-membered rings within the tautomers have a small anti-aromatic character, which is responsible for the longest wavelength absorption. A pronounced anti-aromatic character is characteristic for the enolate ion of phenylazo-1,3-indandione, which should absorb at about 700 nm.

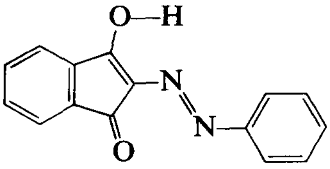
1 INTRODUCTION

Some data have recently been published on the synthesis and absorption spectra of phenylazo-1,3-indandiones **I**.[1] Depending on the substituents and the solvent, these compounds exhibit an azoenol–hydrazone tautomerism. The azoenol tautomer **Ib** absorbs in the range between 396 nm and 413 nm,

Dyes and Pigments 0143-7208/92/$05·00



Ia



Ib

and the hydrazone form **Ia** has absorption maxima between 425 nm and 454 nm.[1] In more nonpolar solvents, the content of the azoenol tautomer is increased.

In general, for hydroxy-substituted azo dyes, the hydrazone form has been reported as the more stable tautomer compared to the azo tautomer.[2-5] Normally, aromatic phenylazo compounds absorb at about 450 nm (n–π^* transition) and at about 320 nm (π–π^* transition).[6] The n–π^* transition is responsible for the deep color of azobenzenes. Annelation of benzene rings at the phenyl residues is connected with a bathochromic shift of the π–π^* transition.[6] A quantum chemical interpretation of the absorption spectra of azobenzene has been given.[6,7] *o*- and *p*-Hydroxy-substituted azobenzenes absorb at 325 nm and 349 nm (π–π^* transition) in ethanolic solution.[6] In the classical theory, the chromophore of azo dyes is the azo group.

In compound **I** there is a five-membered ring within the 1,3-indandione which can have more or less the features of a cyclopentadienyl cation (CPC). The antiaromatic CPC fragment is known as a chromophore in some dyes[8-11] which have long-wavelength absorptions. For the enolate ion of 1,3-indanione all the features of an anti-aromatic character of the five-membered ring have been found.[12] Therefore, in the case of compound **I**, and especially in alkaline solutions of this compound, the chromophore may be the anti-aromatic CPC fragment. We report here the results of quantum chemical investigations of the tautomeric structures of phenylazo-1,3-indaniones and of their enolate ion.

2 INVESTIGATION METHODS

The molecular structures were optimized in relation to their total energy starting with standard geometries by the semi-empirical quantum chemical method MNDO.[13] For these calculations a program package MOPAC[14] was used. The electronic transition energies were calculated using the PPP method[15] based on the MNDO optimized geometries. Previously published atomic and bonding parameters were used.[16] The configuration interaction includes the singly excited configurations constructed from the six highest occupied MO and from the six lowest unoccupied MO.

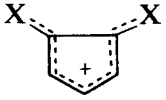
3 CRITERIA FOR THE ANTI-AROMATIC CHARACTER OF THE CPC FRAGMENT

A detailed description of the anti-aromatic character of the CPC is given elsewhere.[8,9,11,12] Here, only the most important criteria are summarized. In addition to a long-wavelength absorption, the following three characteristic features determine the anti-aromatic behaviour:

(i) Geometry criterion
A second-order Jahn–Teller effect influences the ideal D_{5h} symmetry of the CPC and leads to a considerable distortion of the geometry. In the case of heterocyclic analogs of CPC and of substituted CPC, a pseudo-Jahn–Teller effect is operative and leads to a significant bond length alternation and anomalously long bonds within the ring.

C_{2v}

D_{5h}



C_{2v}

(ii) Excitation energy criterion
The derivatives of CPC have small excitation energies (long-wavelength absorption) of the π–π^* transition. In contrast to aromatic systems, an increase of the conjugated π-electron system (by substitution or by annelation of benzene rings) results in a hypsochromic shift of the absorption band, and not in a bathochromic shift as is found for aromatic structures.

(iii) Charge criterion
The localization of the positive charge at the atoms of the five-membered ring is a further qualitative feature for anti-aromaticity. The sum of the net π-electron, the charges Q of the carbon atoms within the five-membered ring of the CPC is $Q = 1$. For derivatives this value is smaller than 1 $(o < Q < 1)$.

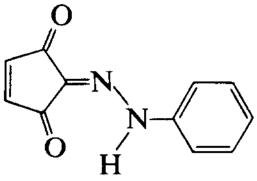
These criteria were applied in evaluations of the absorption spectra of compound **I** and of the enolate ion.

4 RESULTS AND DISCUSSION

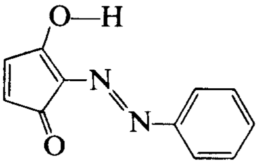
The tautomers **Ia** and **Ib**, and also the corresponding forms with a smaller π-electron system **IIa** and **IIb**, do not have planar configurations. The phenyl rings are strongly distorted about the N(azo)-C(phenyl) bond (**Ia**: 69°, **Ib**: 78°,

IIa: 66°, **IIb**: 24°). However, this distortion does not significantly influence the longest-wavelength absorptions. In contrast to previous conclusions, the azoenol tautomer **Ib** has been calculated to be more stable than the hydrazone form by 0·35 eV (about 34 kJ). Any intramolecular H-bonding within the azoenol tautomer does not significantly influence either the geometry or stability; the energy difference between the H-bonded stabilized form and the nonstabilized tautomeric form is about 14 kJ. The longer-wavelength absorption (432 nm) has been previously assigned to the hydrazone tautomer and the shorter-wavelength absorption (404 nm) to the azoenol form.[1] The results of our PPP calculations show that the azo tautomer has a longer-wavelength absorption than the hydrazone form (see Table 1).

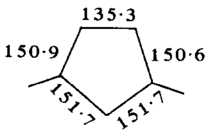
The tautomers of the phenylazo-1,3-cyclopentendione **IIa** and **IIb** with a smaller π-electron system have also been considered in order to examine the criteria of the anti-aromatic character of the chromophore of **I**. The geometries of the five-membered rings of the tautomers of **I** and of **II** show a significant bond length alternation with anomalously long bonds for π-electron systems (MNDO results, bond lengths in pm):



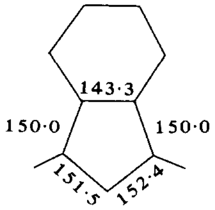
IIa



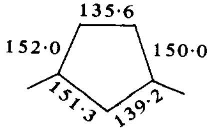
IIb



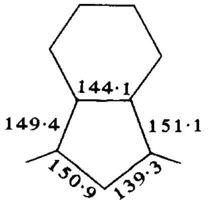
IIa



Ia



IIb



Ib

TABLE 1

Experimental (λ_{max}(exp)) and Calculated (λ_{max}(calc)) Absorption Maxima (in nm) and Calculated Oscillator Strengths (f) of the Tautomers of Phenylazo-1,3-indandiones

p-*Phenyl substituent*	*Hydrazone form* ***Ia***			*Enolazo form* ***Ib***		
	λ_{max}(*calc*)	f	λ_{max}(*exp*)[a]	λ_{max}(*calc*)	f	λ_{max}(*exp*)[a]
H	343	0·152	404	446	0·369	432
	322	0·621	—	292	0·443	—
	253	0·077	—	244	0·043	—
	247	0·034	—			
	229	0·044	—			
CH_3	383	0·868	402	477	0·573	438
Cl	384	0·872	404	477	0·574	436
Br	381	0·867	406	476	0·575	437
OEt	391	0·774	—	484	0·571	454

[a] As pointed out in the text a reversed association with the absorption maxima of the two tautomeric forms has been used in relation to Ref. 1.

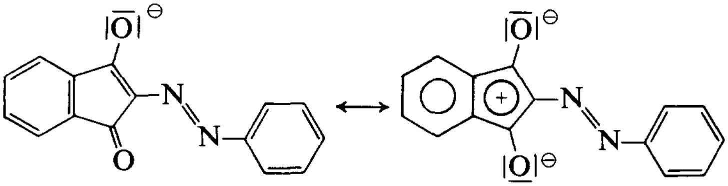
For both tautomeric forms **Ia** and **Ib**, a hypsochromic shift is calculated for structures **IIa** and **IIb** in relation to the smaller π-electron systems **Ia** and **Ib**, respectively (see Table 2). In Table 2 are also summarized the sums of the electronic net changes of the carbon atoms within the five-membered rings of **I** and **II**. The larger values for the structures **IIa** and **IIb** in relation to **Ia** and **Ib** go parallel with longer-wavelength absorption for the smaller π-electron systems **II**. In alkaline solution, compound **I** should form the azoenolate ion structure. In this structure the anti-aromatic character must be increased.[12] The absorption spectra of phenylazo-1,3-indaniones in alkaline solution were not reported in previous studies.[1]

Based on the MNDO optimized geometries, the excitation energies and oscillator strengths have been calculated by the PPP method for structures **Ic**

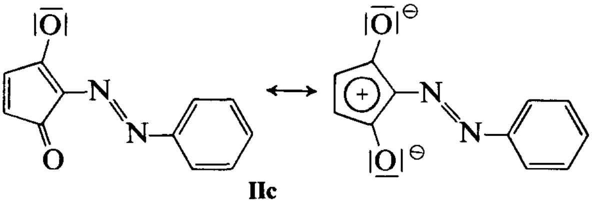
TABLE 2

Comparison of the Calculated (PPP) Longest-wavelength Excitation Energies (λ_{max}(calc) in nm) and of the Sums of the Net π-Electron Charges (Q^{π}(PPP) and Q^{π}(MNDO)) of the Carbon Atoms within the Five-membered Rings of the Structures **I** and **II**

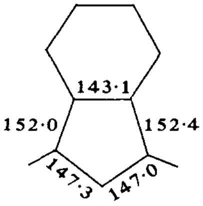
	Ia	***IIa***	***Ib***	***IIb***
λ_{max}(calc)	343	401	446	585
Q^{π}(PPP)	0·390	0·458	0·230	0·272
Q^{π}(MNDO)	0·373	0·438	0·086	0·201



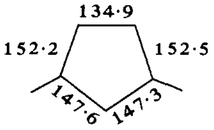
Ic



IIc



Ic



IIc

and **IIc**. The results are shown in Table 3. There is a significant hypsochromic shift of about 220 nm if the conjugated π-electron system is increased from **IIc** to **Ic** by about 220 nm. Also the geometries of the five-membered rings in **Ic** and **IIc** show the typical features of the anti-aromatic structure of the CPC. The total net π-electron charges of the five-membered

TABLE 3

Calculated (PPP) Excitation Energies (λ_{max}(calc) in nm) for the Azoenolate Ions of Phenylazo-1,3-indandione **Ic** and of Phenylazo-1,3-cyclopentendione **IIc**

IIc		*Ic*	
λ_{max}(*calc*)	*f*	λ_{max}(*calc*)	*f*
716	0·086	493	0·191
393	1·008	411	0·942
309	0·069	319	0·170
240	0·037	303	0·074
		249	0·103
		236	0·021

rings are 0·156 (0·398) for **Ic** and 0·157 (0·369) for **IIc**, calculated by the MNDO method (values in brackets: results of PPP calculations).

ACKNOWLEDGEMENT

The authors acknowledge the support of the Fonds der Chemischen Industrie.

REFERENCES

1. Hocaoglu, N., Uyar, T. & Türker, L., *Dyes Pigm.*, **12** (1990) 187.
2. Buraway, A., Salem, A. G. & Thompson, A. R., *J. Chem. Soc.* (1952) 4793.
3. Yagi, G., *Bull. Chem. Soc. Jpn*, **37** (1964) 1875.
4. Simov, D. & Stoyanov, S., *J. Mol. Struct.*, **19** (1973) 255.
5. Bigelow, R. W., *J. Phys. Chem.*, **80** (1976) 2694.
6. Fabian, J. & Hartmann, H., *Light Absorption of Organic Colorants*. Springer-Verlag, Berlin, 1980.
7. Sühnel, J., Thesis, Technical University Dresden, 1975.
8. Tyutyulkov, N., Olbrich, G. & Dietz, F., *J. Inf. Rec. Mater.*, **16** (1988) 431.
9. Dietz, F., Tyutylkov, N. & Tadjer, A., *J. Inf. Rec. Mater.*, **17** (1989) 251.
10. Gompper, R. & Wagner, H.-U., *Angew. Chem.*, **100** (1988) 1492.
11. Tyutyulkov, N. & Dietz, F., in preparation.
12. Tyutyulkov, N., Tasseva, M. & Georgiev, E., *J. Prakt. Chem.*, **329** (1987) 780.
13. Dewar, M. J. S. & Thiel, W., *J. Amer. Chem. Soc.*, **99** (1977) 4899.
14. Stewart, J. J. P., MOPAC 6.00, QCPE No. 455.
15. Hartmann, H. & Merseburg, T. H., PPP program System for PC.
16. Hartmann, H. & Fabian, J., *Ber. Bunsenges. Physik. Chem.*, **73** (1969) 107.