Benzo-1,2,3,4-tetrazine 1,3-dioxides as new chromophore systems

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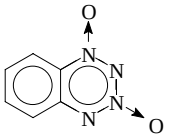
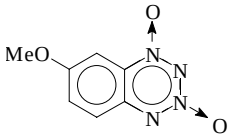
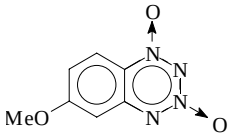
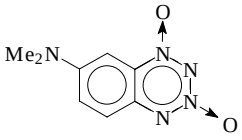
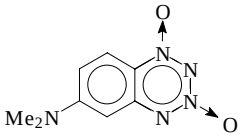
As a result of an experimental and theoretical study of the electronic absorption spectra of benzo-1,2,3,4-tetrazine 1,3-dioxides, electron transitions in the tetrazine dioxide fragment have been identified and the influence of substituents in the benzene ring on the positions of bands has been elucidated.

As a rule, azoxy-compounds exhibit no absorption bands in the visible region.[1,2] For example, the long-wavelength absorption bands in the UV spectra of *cis*- and *trans*-azoxybenzene are located at 323 and 327 nm, respectively.[3] However, benzo-1,2,3,4-tetrazine 1,3-dioxides (BTDO) in which two azoxy-groups are directly bound to each other are coloured from yellow to violet depending on the position of the substituent in the benzene ring. Therefore, in our opinion, it would be of considerable interest to study the electronic spectra of these compounds in order to identify the absorption bands related to the new chromophore system of BTDO.

The present paper is devoted to an interpretation of the electronic absorption spectra of BTDO[†] and to an elucidation of the influence of substituents in the benzene ring on the positions of bands corresponding to transitions localised in the tetrazine dioxide fragment.

The bands in the electronic spectra of BTDO were assigned based on experimental[‡] and theoretical data. While calculating by means of the CNDO/S method[5,6] interaction of 60 singly excited configurations corresponding to the transfer of an electron from each of the ten higher occupied molecular orbitals to each of the six lower unoccupied molecular orbitals was taken into account. Interpretation of the electronic spectra of BTDO has shown that the bands localised in the regions of 300–390 nm and 408–545 nm are due to the π–π* and n–π* transitions in the tetrazine dioxide fragment, respectively (Table 1). The bands at 200–300 nm are due to transitions with intramolecular charge transfer from the π orbital of the tetrazine dioxide fragment to the antibonding orbital of the benzene ring and from the π orbital of the benzene ring on the antibonding orbital of the tetrazine dioxide fragment. These bands are intense (ε *ca.* 10^4–2×10^4).

Table 1 Absorption bands due to the tetrazine dioxide fragment in the UV spectra of benzo-1,2,3,4-tetrazine 1,3-dioxides (**1a**–**1e**) in methanolic solution.

Compound	Structural formula	Transition	Experiment		Calculations	
			λ_{max}/nm	ε^a	λ_{max}/nm	f^b
1a		π–π*	310[c]		327	0.2033
		n–π*	420	1700	416	0.00005
1b		π–π*	337	7000	330	0.07
		n–π*	453	3200	397	0.0009
1c		π–π*	300[c]		334	0.28
		n–π*	408	3300	441	0.00006
1d		π–π*	388	9300	383	0.13
		n–π*	545	2200	440	0.00001
1e		π–π*	345	3500	338	0.31
		n–π*	470	2700	449	0.0001

[a]Extinction coefficient ($dm^3\ mol^{-1}\ cm^{-1}$). [b]Oscillator strength. [c]Inflection.

[†] The synthesis of BTDO **1a** has been reported previously,[4] and the synthesis of **1b**–**1e** will be reported later.

[‡] The UV spectra of BTDO were recorded on a Specord UV/VIS spectrophotometer in methanolic solutions by standard procedures.

The introduction of an Me_2N group into the 7-position of the molecule **1a** results in a larger bathochromic shift (78 nm) of the band corresponding to the π–π* transition in the tetrazine dioxide fragment than the introduction of an MeO group; this implies that in the molecule containing a stronger donor, the bonding and antibonding π orbitals are closer to each other. However, the bathochromic shift following the introduction of an Me_2N group into the 6-position is much smaller (35 nm), and an MeO group introduced into the 6-position even leads to a slight hypsochromic shift of this band (Table 1).

The above substituents introduced into the 7-position cause a substantial bathochromic shift of the band corresponding to the n–π* transition. For the Me_2N-containing derivative, this shift is 125 nm. However, the bathochromic shift following the introduction of an Me_2N group in the 6-position is much smaller (50 nm), and the introduction of an MeO group in this position leads to a slight hypsochromic shift of the n–π* transition band.

Thus, electron-donating substituents in the 7-position cause markedly more pronounced changes in the region of the UV spectrum containing the bands, which correspond to electron transitions in the tetrazine dioxide fragment than the same substituents in the 6-position. At the same time, it is noteworthy that the electron-donating properties of MeO and Me_2N groups are more pronounced in the 6-position. This can clearly be seen from the charges on the atoms in the tetrazine dioxide fragment found by MNDO calculations.[7]

Thus, the study of the UV spectra of BTDO made it possible to identify the absorption bands corresponding to the transitions in the tetrazine dioxide fragment and to interpret the transitions responsible for the colour of BTDO.

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