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Spectroscopic Investigation of Some Chalcones

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Spectroscopic Investigation of Some Chalcones

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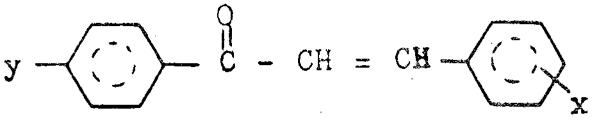
The electronic absorption spectra of some chalcone derivatives are recorded in organic solvents of varying polarities. The absorption bands within 215–256 and 255–305 nm range are assigned to $\pi - \pi^*$ transition of the aromatic rings while the band within the 290–365 nm is assigned to C.T. interaction within the whole molecule. The C.T. origin of this band is supported by calculating the energy of the C.T. interaction. The shift of C.T. band is discussed in terms of medium and substituent effect. The ir–spectra are recorded in the solid state as KBr discs, and the main bands are assigned. The C=O and CH bands were found to be influenced by changes of substituent on the arylidene ring, however, only the C=O band displayed linear $\nu - \sigma$ (Hammett constant) plots. The H nmr spectra in CCl_4 are also discussed.

Chalcones are intresting class of compounds so far their synthesis, structure and photochemical behaviour are concerned. Though many investigations delt with these compounds, yet few studies considered the spectral behaviour of such compounds. It seems also that the only systematic investigation on the spectral behaviour of chalcones is that considering their ir–spectra[1].

In the present investigation, the electronic absorption spectra of some chalcones are recorded in organic solvents of varying polarities. The absorption bands are assigned to corresponding electronic transitions; the effect of substitution at the phenone and arylidene rings and solvent effect are studied. Also the effect of substituents on the C=O band in the ir–spectra is considered.

The compounds included in the present investigation have the general structural formula:



in which y = H (I) or CH_3 (II)

x = p–$N(CH_3)_2$ (a), p–OCH_3 (b), o–OH (c), p–OH (d), H (e), p–Cl (f), p–NO_2 (g), also furfurylidene (h), cinamylidene (i) and dioxymethylenephenyl idene (j) derivatives are considered.

EXPERIMENTAL

The chalcones under investigation were prepared by condensation of acetophenone or p–methylacetophenone with benzaldehyde derivatives as recommended before[2]. The compounds obtained were purified by repeated crystalization from appropriate solvent.

The working procedures and apparatus are the same as given previously[3].

RESULTS AND DISCUSSION

I– UV spectra:

The ultraviolet spectra of the chalcones considered in the present work are recorded in organic solvents of various polarities. The spectra in solvents transparent in the region below 300 nm, viz ethanol, ether or cyclohexane display generally three bands while other solvents e.g. CCl_4 or $CHCl_3$ give only one absorption band (Fig. 1).

a) Band assignment (Table 1)

The three bands observed in ethanol, ether or cyclohexane spectra lie within the 215–250, 257–305 and 298–362 nm ranges. The first band corresponds to the medium energy $\pi - \pi^*$ transition of the aromatic rings. The band splits in the nonpolar solvent cyclohexane indicating a composite nature of the band[3]. The second band can be assigned to the low energy transition of the aromatic ring overlaping with that due to the $\Phi \rightarrow C=O$ interaction. The composite nature of this band is gathered from its splitting in some solvents for compounds with strong donor substituents. In the spectra of compounds with acceptor substituents and IIa, this band is masked by the intense longer wavelength band. The longer wavelength band is not observed in the spectra of either acetophenone or benzaldehyde derivatives; this band can be assigned to an intramalecular charge transfer interaction. The interaction involves probably the location of a π–electron from the arylidene ring (as donor) on the $C=O$ group as acceptor. The mesomeric shift which corresponds to this C.T. interaction can be represented as follows:

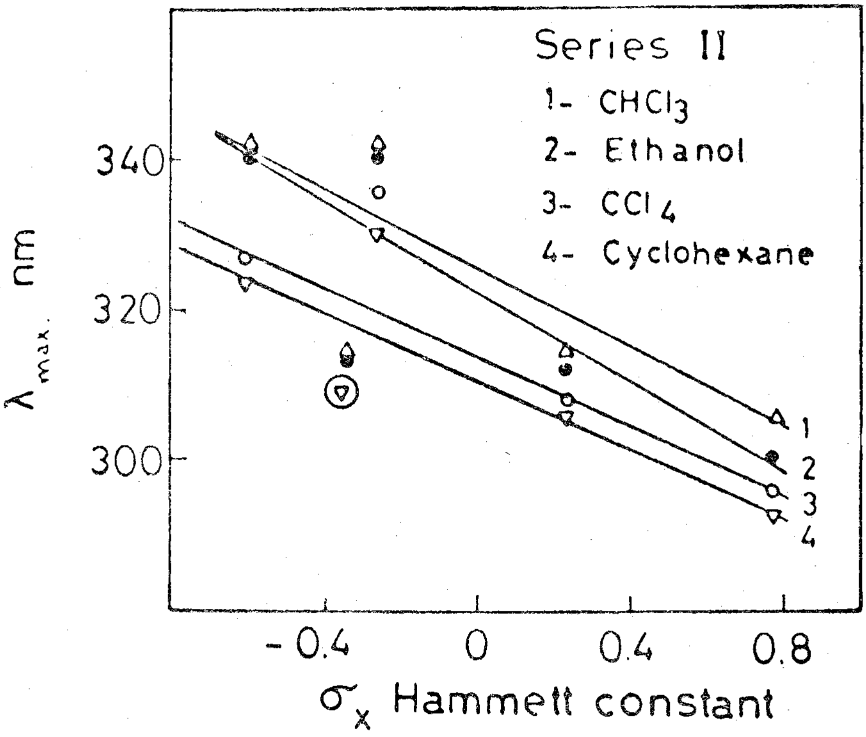


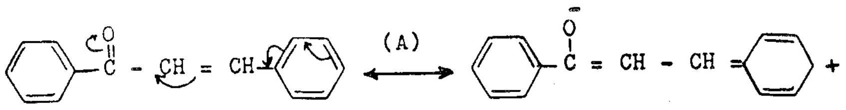
Fig. 1. Relation between λ_{max} and σ_x–Hammett constant.

Table 1. Results obtained from uv-spectra in ethanol.

		$\pi - \pi^*$		π-π^* + ∅-C=O		C.T.	
No.	σ_X	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Results for series I: (ρ = 35 nm, r = 0.87)							
a	-0.60	245	1.29	268	0.78	343	2.66
b	-0.27	242	1.44	292	1.23	343	1.93
				270	1.26		
c	——	228	1.43	270	1.09	355	1.15
				257	1.25	302	1.53
e	0.00	228	1.36	260	1.05	309	2.25
f	0.23	243	1.85	277	1.16	305	0.45
g	0.78	225	1.63	——	——	302	3.32
i	——	233	1.06	265	1.02	349	2.45
j	——	233	2.16	293	0.96	362	2.06
				265	1.66		
Results for series II: (ρ = 26 nm, r = 0.81)							
a	-0.60	242	1.41	305	1.06	340	2.03
b	-0.27	250	1.85	305	0.73	340	1.46
				290	0.52		
d	-0.36	232	3.69	278	2.03	313	2.11
f	0.23	230	1.56	270	1.41	312	1.60
g	0.78	215	1.91	——	——	300	2.09
h	——	230	1.96	273	0.90	337	2.27
i	——	215	1.90	300	0.87	355	1.31
				265	1.38		

——: masked by C.T. band.

λ_{max} nm, ε_{max} (mol l cm^{-1} x 10^{-4})



The C.T. character of this band is gathered from its broad envelope and high molar extinction[4]. A further support for this can be gained by calculating the C.T. energy of this interaction for compound Ig using the relation:

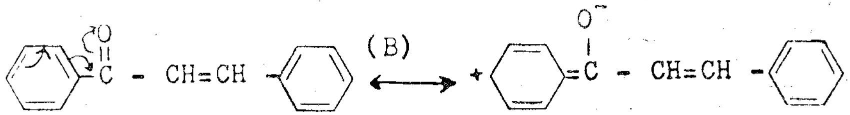
$$E_{C.T.} = I_p - (E_f + C)$$

where I_p : ionisation potential of the donor part (taken as that for benzene 8.90 eV)[5]

E_f : electron affinity of the C=O group (-1.40 eV)[6]

C : coulombic force between the electron transfered and the positive hole left behined (5.7 eV).

The value calculated (4.6 eV) is not much different from that determined from λ_{max} in cyclohexane (4.16 eV). The somewhat higher values for E_{CT} calculated can be ascribed to the existence of the CH=CH system conjugated with the aromatic ring which causes a lowering of the ionisation potential of the donor system x-∅-CH=CH-. The λ_{max} value corresponding to 4.50 eV amounts to 270 nm. The conjugation with the C=C causes a shift of 35 nm (amounts to 40 nm, from a comparison of e with i) hence λ_{max} should be near 305 nm for the C.T. interaction. The lower value in cyclohexane (298 nm) can be explained on the basis that the C.T. interaction in (A) is antagonised by the charge migratiom according to (B), thus:



This antagonising effect is gathered from the blue shift of the C.T. band on going from series I to series II. The increased antogonising effect in II is due to the higher donor character of the tolyl group in comparison to the phenyl ring. Thus the C.T. effect would involve the whole molecule.

b) **Substituent effect:**

The bands corresponding to the $\pi - \pi^*$ transitions of the aromatic rings display small irregular shifts with changed nature of the substituent. This behaviour is common among substituted benzenes. On the other hand, the C.T. band shows a regular shift to longer wavelength with increased donor character of the substituent (x) compared to the nonsubstituted compound. Acceptor substituents cause a blue shift which increases from Cl to NO_2 derivative. This behaviour substantiates the assumption given before that the arylidene ring would be the origin of the C.T. interaction.

The plot of λ_{max} as a function the σ – (Hammett) constant (Fig. 1) is a more or less linear relation for series II. This denotes the validity of the Hammett equation in the form:

$$\lambda_x = \lambda_H + \rho\,\sigma_x$$

to the C.T. interaction in the chalcones under investigation. The ρ–values amount to 35–23 nm for (I) and 26–22 nm (II), the correlation coefficients are 0.91–0.80 for (I) and 0.84–0.75 for (II) respectively. On comparing the spectra of e, h, i and j it is observed that the C.T. band shifts to red in the order (e → h → i → j). The lowest C.T. energy with j results from the existence of the donor part on a condensed ring system with a heterocyclic ring. As a matter of fact, condensed ring system have lower ionisation potentials compared to single rings. Also the heterocyclic system lowers further the ionisation energy. The red shift from e to h is due to the lower ionisation energy of the furan or furfural compared to benzene and benzaldehyde[5]. The shift to lower energy in case of i compared to e or h results from the increased conjugation in the molecule.

c) Solvent effect (Table 2 & Fig. 2)

The bands of the $\pi - \pi^*$ transitions of the aromatic rings shift to red with increasing solvent polarity which is a common behaviour for these transitions[4]. The C.T. band generally shifts to red with solvent polarity though few exceptions occur. The irregularity generally occurs with compounds containing substituents having high solvation properties. Thus chalcones display a positive solvato chromic effect.

To test solvent effect, the spectra of Ie (where no substituents exist on the aromatic rings) are recorded in eleven different solvents having varied polarities (Fig. 2 shows seven of these solvents). The application of Gati and Szalay equation[7] to the system under investigation did not give satisfactory linearity for the plots. This is also the case for the dielectric functions given by Suppan[8]. The same holds for all compounds in the five solvents investigated (Tables 1 & 2). This behaviour indicates that the dielectric constant of the medium, though having an important role in solvent effect, is not the only factor governing the band shift. Other factors contributing to band shift would be

Table 2. Results obtained for the C.T. band in different solvents.

No.	Chloroform		Ether		CCl_4		cyclohexane	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
	Results for series I:							
a	339	3.46	329	2.64	330	4.17	325	4.88
b	338	2.14	——	——	333	2.30	332	2.34
c	340	1.16	342	1.40	335	...	337	...
	302	1.46	298	1.74	303	...	302	...
e	308	1.74	302	2.17	305	2.31	298	1.21
g	302	2.80	296	....	296	3.73	295	....
i	348	2.42	....	....	342	2.47	337	2.88
j	355	2.14	346	2.33	349	2.69	344	2.64
	(29,0.88)		(23,0.91)		(27.5,0.88)		(25.0.80)	
	Results for series II:							
a	340	55.08	328	3.83	327	2.52	324	3.09
b	341	2.24	——	——	335	2.47	330	2.40
d	313	1.38	——	——	309	....	309	....
f	313	1.98	——	——	308	2.05	306	2.12
g	305	2.18	297	1.99	296	2.32	292	2.38
h	340	2.26	330	3.07	334	1.20	329	2.09
i	342	2.88	——	——	336	2.88	331	4.47
j	353	1.83	345	1.89	347	2.07	343	2.33
(ρ,r)	(23,0.75)		——		(22,0.77)		(23,0.84)	

——: not recorded, ...: saturated solution used.

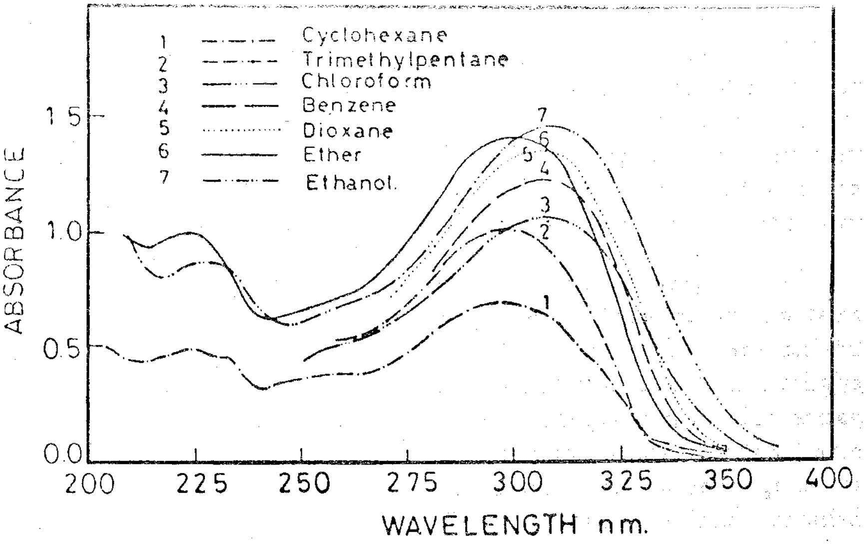
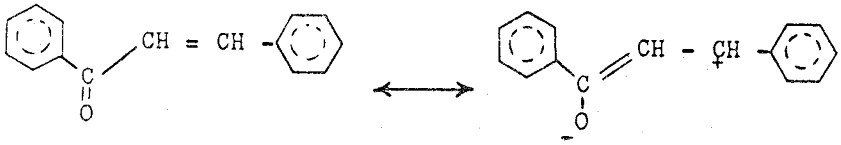


Fig. 2. Electronic absorption spectra of Ie in different organic solvents.

the change of solvation of the ground and excited states[9] as well as solute–solvent interaction through hydrogen bonding[10] especially in ethanol solutions.

Recourse was taken to investigate the change of the C.T. band position as a function of some solvent parameters. The solvents used in the present investigation differ in their ability of donating and accepting protons in their interaction with solute molecules. The position of λ_{max} shows no linear correlation with the D_N or Z parameters indicating that most solvents used cannot function in the solvation process as proton donors to solute. The plot of λ_{max} as a function of A_N or E_T is a more or less linear relation with apparent deviation for ethanol. This denotes that solvation with these solvents would essentially take place through such type of bonding that involves electron transition or proton from the solute molecule. The chalcone molecule with a conjugate π–electronic structure can be described in terms of the mesomeric structures:



The chalcone molecule exhibit some active centers for solvation including the nucleophilic center on the C=O group. Electron acceptor parts of the aprotic solvents can readily interact with the nucleophilic center of the molecule through an electrophilic attack.

As gathered from the λ_{max} –A_N plots, it can be observed that solvents with electron accepting character lie more or less on the linear relation whereas those solvents acting as electron donating ones deviate from this linearity. The high deviation with ethanol is due to the fact that this solvent can behave as electron donor through the oxygen lone pair as well as electron acceptor through the hydroxyl proton leading to intermolecular hydrogen bonding. The small size of ethanol molecules and their varied mode of interaction favours a higher solvation number for this solvent alternatively a higher solvation enerygy compared to other solvents hence the larger shift to red. This behaviour supports that the main shift in λ_{max} of C.T. band would be ascribed to solute–solvent interaction involving hydrogen bonding where the solvent molecules would behave as proton donor or acceptor.

II. The ir-spectra:

The important bands in the ir–spectra of the compounds included in the present investigation are assigned considering the bands characteristic of substituted benzenes.

The two low intensity bands within the 3120–3080 cm^{-1} and 3060 –3040 cm^{-1} ranges correspond to the asym. and sym. stretching vibrations of the aromatic C–H bonds. The band at 3030–3010 cm^{-1} is assigned to the C–H stretching of the =C–H group[12]. The apparently intense bands within the 1685–1650 cm^{-1} range is due to the stretching mode of the C=O linkage. This band generally shifts to higher wavenumber as the acceptor character of the substituent on the arylidene ring increases. The three intense to medium bands with the 1610–1570 cm^{-1} are assigned to the vibrations of the aromatic ring. The inplane deformation of the =C–H bond leads to the broad weak band at 1460 –1430 cm^{-1}. The band generally shifts to higher values as the acceptor character of the arylidene system increases. The inplane bend of the aromatic C–H groups leads to a group of 3–5 sharp medium intensity bands near 1180, 1150, 1100, 1020 and 880 cm^{-1}. The number of bands increases as the difference in electronic character between the substituents on the two aromatic rings increases. This results from the increased difference in the energy state of the two molecules as a result of the changed charge density on the rings. The medium or high intensity bands below 900 cm^{-1} charcterise the type of substitution of the aromatic rings. For series I, the bands due to the monosubstituted ring appear as a strong band at 755–735 cm^{-1} and a medium one at 710–690 cm^{-1}. The bands for the p–disubstituted rings of a, b, d, f and g lie at 800–820 and 790–780 cm^{-1}. These bands overlap with those of the p–tolyl group of series II. For compounds of series II, the bands appear in case of acceptor substituents as doubled band or a band and a shoulder. For compound c with the OH–group in o–position to the other group, the γ_{CH} band appears quite intense near 735 cm^{-1}. For compound e and i the γ_{CH} bands of the arylidene ring overlap with those of the phenone ring in case of series I while for II they are observed near 750 and 695 cm^{-1}.

Generally, the γ_{CH} bands of both rings display apparent shifts with changed electronic character of the substituents of the arylidene ring. Though the shifts are not regular yet it indicates that the changed charge density on the arylidene ring has its effect on the electron density on the other ring.

The plot of the band position as a function of the σ_x–Hammett constant gives a more or less linear relation in case of the C=O band only. The ρ–values amount to 15 and 18 cm^{-1} for I and II respectively. The line for series II lies at lower values than that for I which results from the presence of the donor CH_3–group on the phenone ring (Fig. 3).

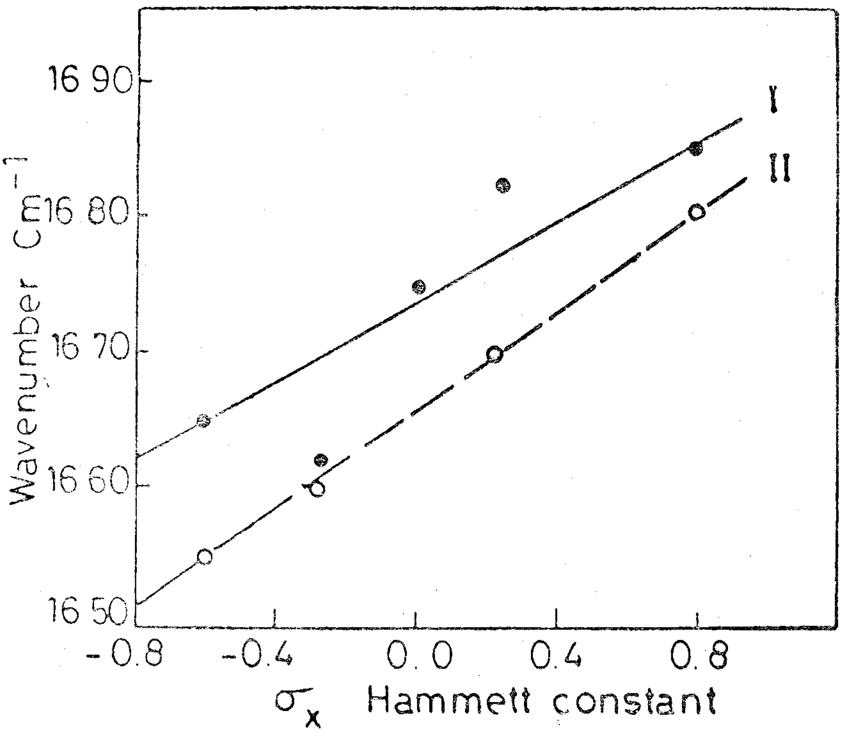


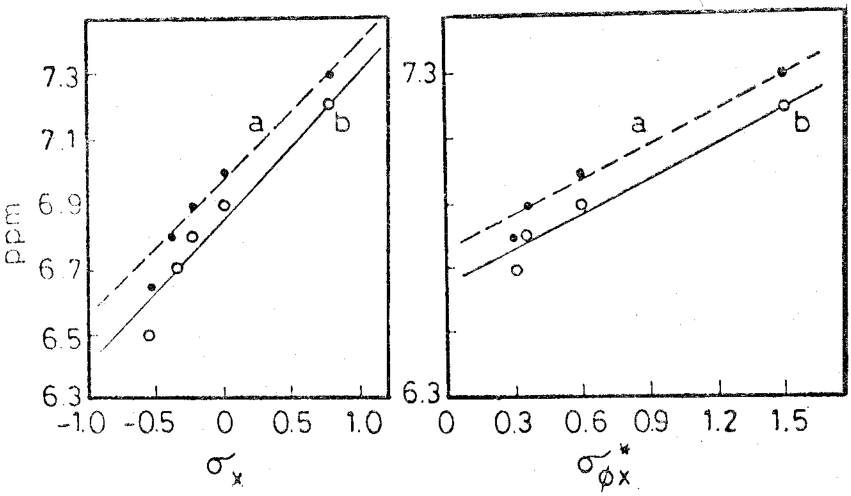
Fig. 3. Relation between $\nu_{C=O}$ and σ_x – Hammett constant I–series (I), II–series (II).

III. The ^1H nmr spectra:

The ^1H nmr spectra of the chalcones under investigation measured in CCl_4 as solvent display the signals characterising the protons of the phenone moiety at 8–7.4 ppm. The integration value of these signals corresponds to five protons for I and four protons for II. The position of these signals is but slightly influenced by changed nature of the substituent on the arylidene ring (x) but is shifted to lower fields on going from I to II.

The protons of the benzylidene ring lead to a group of signals within 7.8–7.1 ppm region which are influenced by changed nature of the substituent in this ring. These signals shift to higher fields as the acceptor character of the substituent (x) increases.

The two protons of the methylene linkage lead to the doubled signals within the 7.3–6.4 ppm range, each of which has an integration value corresponding to one proton. The higher field signal is assigned to the proton near the phenone ring while the lower field is that for the proton near the benzylidene ring. The position of these protons is influenced by the nature of the substituent on both rings. The plot of the signal values as a function of the σ_x or the $\sigma_{\varnothing x}$ of the substituent (x) is a more or less linear relation (Fig. 4) denoting the validity of the



Fif. 4. Effect of substituent on the position of the $\varnothing$–CO–CH=CH–$\varnothing$ protons. (a) asetophenone proton (b) benzylidene proton.

Hammett linear free energy relationship to the system under investigation. The same holds for the $\delta - I_p$ values of the benzal ring taken as those of the corresponding benzene derivatives denotiag that the shift of the signals is governed by charge transfer from the arylidene ring to the methylene linkage.

In addition to these signals, the protons of the CH_3 groups of II lead to a signal near 2.4 ppm, those of the OCH_3 group of b near 3.8 ppm and those of the $-N(CH_3)_2$ near 3.0 ppm. The shift in these signals to higher fields as the electronegativity of the atom attached to the CH_3 group increases.

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