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The electronic absorption spectra of the alkyl-substituted derivatives of bis(benzene)chromium(0) in the vapour phase

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Abstract

The UV and visible absorption spectra of (arene)$_2$chromium(0) (arene = benzene (I), toluene (II), ethylbenzene (III), cumene (IV), tert-butylbenzene (V), mesitylene (VI)) in the vapour phase have been investigated. Four band systems A, B, C and D are revealed in the spectra. The bands of the system with the shortest wavelengths, D, represent the Rydberg series. The first ionisation potentials $IP_{a_{1g}}$ of I–VI determined from the Rydberg band frequencies are 5.45, 5.29, 5.25, 5.21, 5.18 and 5.01 eV respectively. The Rydberg bands correspond to the allowed electrodipole transitions from the highest occupied molecular orbital (MO) a_{1g} to the vacant MO of either the a_{2u} or e_{1u} type.

System C corresponds to the intense band of the solution spectra. The electronic transition $e_{2g} \rightarrow e_{2u}^{\star}$ obviously makes a great contribution to this system. System B is assigned to the transition from a_{1g} to vacant a_{2u} or e_{1u} MO, which can be Rydberg orbitals. System A can be assigned to the $a_{1g} \rightarrow e_{2u}^{\star}$ transition or to the Rydberg transition, which is forbidden in the D_{6h} point group but becomes allowed upon reduction of symmetry.

Introduction

The UV and visible spectra of the bis(arene)chromium(0) complexes, in contrast with the spectra of their cations, have been little investigated. The absorption spectra of bis(benzene)chromium(0) in the vapour phase [1] and in solution [2,3] have been found, with little correlation between them. Assignment of the bands in the vapour-phase spectrum [1] was made at a time when photoelectron spectroscopy data on the occupied molecular orbitals (MO) of the complex was not available.

So it was of interest to us to investigate the electronic absorption spectra of the alkylsubstituted derivatives of bis(benzene)chromium(0) in the vapour phase and to compare them with those obtained in solutions and with the results of photoelectron spectroscopy [4,5]. Since the ionization potentials from the highest occupied MO a_{1g}

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($IP_{a_{1g}}$) for these complexes is low, one may expect the appearance of Rydberg series in the spectra, though such a series had not been found previously [1]. Richer and Sandorfy [6] suggested that Rydberg bands made a significant contribution to the vapour-phase far-UV absorption spectra of Fe, Co, Ni biscyclopentadienyl complexes. However, the Rydberg series approaching ionization limits in the spectra of ferrocene, cobaltocene and nickelocene [6] were not observed.

Herein we describe the vapour-phase UV and visible spectra of (arene)$_2$chromium (0) (arene = benzene (I), toluene (II), ethylbenzene (III), cumene (IV), tert-butylbenzene (V), mesitylene (VI)) obtained by us. For comparison, the solution spectra of II and III in n-heptane were recorded.

Experimental

The vapour-phase spectra were recorded by use of a heated vacuum cell on "Specord UV-VIS" (Carl Zeiss, Jena, GDR) spectrometer in the 45000–12500 cm^{-1} region. The temperature was varied from 80 to 170 °C. The solution spectra were recorded on the same spectrometer, in vacuum at room temperature (solvent n-heptane, $c = 1 \times 10^{-3}$–1×10^{-4} mol/l). The error in the band position determination was put at 50–80 cm^{-1} for the narrow bands, and 100–200 cm^{-1} for wide bands and shoulders.

The chromium complexes were prepared by cocondensing organic ligand vapour and metal atoms at liquid-nitrogen temperature [7]. The aromatics used in the synthesis were purified by standard methods [8]. Their purity was controlled by chromatographic methods and the content of main component was found to exceed 99%. All complexes obtained were purified by vacuum sublimation and distillation.

Results and discussion

The vapour-phase spectra of I–VI have many similar features. The absorption band positions in the spectrum of I are consistent with the data in ref. 1. Introduction of alkyl groups into the benzene rings results in a change in the band structure. This appears to be strongest in the spectrum of VI. Nevertheless, every vapour-phase spectrum can be classified into four absorption band systems A, B, C and D (Fig. 1). The solution spectra of II and III (Fig. 2) are clearly different from those of their vapours. Yet, comparison of Fig. 1 and Fig. 2 does show some similarities between the spectra. The strong wide absorption band near 31000 cm^{-1} (Fig. 2) obviously corresponds to system C (Fig. 1). The asymmetric shape of this band may be due to the contribution of the electronic transitions corresponding to system D of the vapour-phase spectra. The shoulders (24400 and 26400 cm^{-1}) in the solution spectra were apparently transformed into systems A and B in the vapour spectra.

The presence of the D system constitutes the greatest difference between the vapour-phase spectra and the solution spectra. This system may be seen as a sequence of bands with well-defined maxima (bands 1–7, Fig. 1), each accompanied by weaker shortwave bands. The intensities of bands 1–7 and the distances between the neighbouring bands of this sequence decrease quickly on transition from the low frequencies to high frequencies. Since the difference between ν_2 and ν_1 is large (about 3200 cm^{-1}), the interpretation that D is the vibrational structure of a single

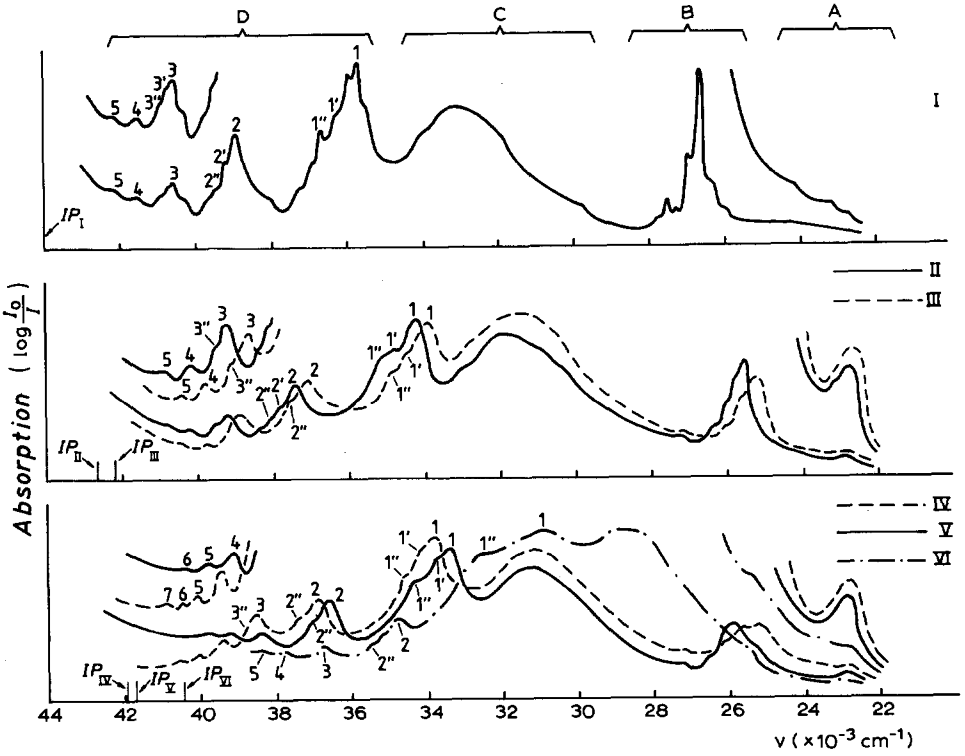


Fig. 1. The electronic absorption spectra of complexes I–VI in the vapour phase. The first ionization potentials (IP_i) are marked on the energy axis.

electronic transition is unlikely. Obviously D corresponds to several transitions.

On the other hand, because $IP_{a_{1g}}$ for $(C_6H_6)_2Cr(0)$ is 5.45 eV, or 43950 cm^{-1} [5], the frequency of any allowed electrodipole transition from the highest occupied MO a_{1g} to the vacant Rydberg MO must be less than 43950 cm^{-1}. Analysis, in fact, shows that the bands 1–7 belong to the Rydberg series, the frequencies of which are described by the Rydberg formula; $\nu = A - R/(n-\delta)^2$ (eq. 1), where A = the

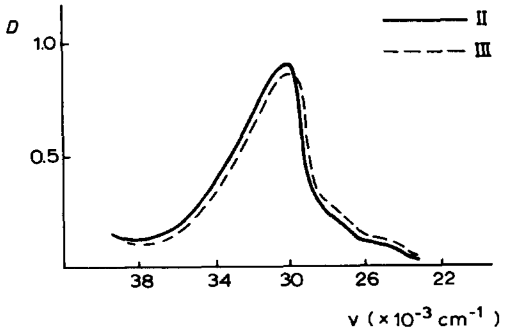


Fig. 2. The electronic absorption spectra of complexes II and III in n-heptane ($c = 1.5 \times 10^{-4}$ mol/l).

Table 1

Rydberg series in the absorption spectra of I–VI. Calculated and experimental band frequencies ν [a] (cm^{-1}), ionization limits A (eV), first ionization potentials $IP_{a_{1g}}$ (eV) (from the photoelectron spectroscopy data), quantum defects δ and n values (see eq. 1) are presented.

Band (Fig. 1)	n [b]	I		II		III	
		ν_c	ν_o	ν_c	ν_o	ν_c	ν_o
1	4	35760	35700	34220	34220	33870	33900
2	5	38920	38880	37500	37460	37150	37160
3	6	40550	40540	39180	39180	38830	38820
4	7	41510	41530	40160	40170	39810	39780
5	8	42120	42140	40860	40800	40430	40440
6	9	42520		41200		40850	
7	10	42810		41490		41140	
δ [b]		0.35		0.40		0.40	
1′	4	36270	36270	34860	34860	34500	34500
2′	5	39170	39150	37820	37840	37450	
3′	6	40700	40780	39360		39000	
δ [b]		0.23		0.25		0.26	
1″	4	36700	36620	35220	35170	34890	34900
2″	5	39380	39420	37980	38030	37650	37620
3″	6	40820	40800	39440	39480	39110	39100
4″	7	41670	41780	40340		39990	39990
δ [b]		0.12		0.16		0.16	
A		5.45±0.01		5.29±0.01		5.25±0.01	
$IP_{a_{1g}}$		5.45 [5], 5.4 [4]		5.24 [4]			

[a] $\nu_c = \nu$ calculated; $\nu_o = \nu$ observed. [b] It is possible that instead of these values of δ and n the values of $(\delta + k)$, and $(n + k)$, where k is an integer must be used.

ionization limit, R = the Rydberg constant, δ = the quantum defect, n = a principal quantum number.

The observed band frequencies and those calculated from eq. 1 are shown in Table 1. A good correlation between the ionization limits obtained for I, II and VI with the first ionization potentials derived from the photoelectron spectra indicates that the suggested assignment is correct. Thus the values of $IP_{a_{1g}}$ determination for bis(arene)chromium(0) complexes from the vapour-phase electronic absorption spectra is possible.

The frequencies of the majority of other bands in system D can also be found if the ionization limits obtained for the first Rydberg series are applied. The correlation of the calculated frequencies with those observed is not as good in this case as compared with the first series (Table 1). This may be explained by insufficient exactness in shoulder position determination. Furthermore, the possibility that these bands can be interpreted as a vibrational structure of the first Rydberg series electronic transitions cannot be entirely excluded. However, assignment of these bands to the second and third Rydberg series should throw light in some features of the intensity distribution. For instance, the increase in the relative intensity of band

1″ (Fig. 1) may be caused by the presence of the third series. The existence of several Rydberg series is quite possible, since even in the case of D_{6h} symmetry of all the complexes considered, there are four groups of Rydberg orbitals: npe_{1u}, npa_{2u}, nfe_{1u}, nfa_{2u} for which the electrodipole transitions from the a_{1g} orbital are allowed.

Table 1 (continued)

IV		V		VI		Rydberg series
ν_c	ν_o	ν_c	ν_o	ν_c	ν_o	
33760	33800	33370	33380	30920	30900	1st
36920	36920	36600	36600	34740	34800	
38550	38560	38270	38300	36650	36640	
39510	39500	39240	39220	37730	37720	
40120	40100	39810	39830	34810	38320	
40520	40500	40260	40280	38860		
40810	40800	40550		39170		
0.35		0.38		0.60		
34130	34130	33800	33800			2nd
37110		36820	36800			
38660		38390				
0.26		0.28				
34550	34560	34300	34280	32730	32680	3rd
37310	37330	37060	37100	35610	35610	
38770	38750	38520	38600	37130	37130	
39640	39720	39390		38020		
0.16		0.16		0.22		
5.21 ± 0.01		5.18 ± 0.01		5.01 ± 0.02		
				5.01 [4]		

Comparison of the bisarene complex ionization limits derived from the absorption spectra shows that the influence of methyl substituents on $IP_{a_{1g}}$ is additive. The introduction of one methyl group into each ring of $(C_6H_6)_2Cr(0)$ decreases $IP_{a_{1g}}$ by 0.16 eV and the introduction of three CH_3 groups into 1,3,5-positions decreases it by 0.44 eV. Thus one may expect the $IP_{a_{1g}}$ of bis(*m*-xylene)chromium(0) to be 5.15 eV. If CH_3 groups replace the H atoms in the CH_3 groups of bis(toluene) chromium(0), then the introduction of one, two and three groups into each fragment causes a decrease in $IP_{a_{1g}}$ by 0.04, 0.08 and 0.11 eV respectively. Moreover, a linear correlation between $IP_{a_{1g}}$ of II–V and the inductive constants $\sigma^\star$ of the corresponding substituents in the rings has been found. The correlation is described by the equation: $IP_{a_{1g}}(\mathrm{eV}) = 5.29 + 0.37\sigma^\star$; $r = 0.996$.

The additive influence of the substituents on $IP_{a_{1g}}$ and the existence of the linear correlation between $IP_{a_{1g}}$ and $\sigma^\star$ confirm that $IP_{a_{1g}}$ decreases with increasing number of alkyl groups introduced into the benzene rings as a result of increased electron–electron repulsion. A similar conclusion was arrived at by Evans et al. [4] on the basis of the I, II, VI photoelectron spectrum analyses.

Table 2

Band positions (cm^{-1}) ^{a} in the A, B and C systems for the complexes I–VI (see also Fig. 1)

I	II	III	IV	V	VI	System
22900 ^{b}	22870m	22940m	22980m	22980m	22400 ^{b}	A
23140 ^{b}	23140 ^{b}					
24080 ^{b}						
26120 ^{b}						B
26440 ^{b}						
26700vs	25530s	25250s	25000 ^{b}	25440 ^{b}	25400 ^{b}	
26940s	25790 ^{b}	25500 ^{b}	25200s	25940s		
27200m	26000 ^{b}		25660s			
27470s	26380 ^{b}	26010 ^{b}	26200 ^{b}	26660 ^{b}		
27760 ^{b}						
29800 ^{b}	30050 ^{b}	29800 ^{b}				C
31800 ^{b}	30760 ^{b}					
32900 ^{c}	31820 ^{c}	31400 ^{c}	31300 ^{c}	31300 ^{c}	28700 ^{c}	
	32870 ^{b}					

[a] vs = very strong, s = strong, m = moderate. [b] Shoulder. [c] Wide maximum.

The difference between $IP_{a_{1g}}$ and the Rydberg transition energy $h\nu_R$ represents a Rydberg state ionization potential IP_R corresponding to the removal of one electron from the occupied Rydberg orbital. Defined this way, IP_R values for the Rydberg state corresponding to band 1 (Fig. 1) are 1.03, 1.06, 1.06, 1.02, 1.04, 1.18 eV for complexes I–VI respectively. The introduction of one alkyl substituent into each ring does not change IP_R significantly, but the introduction of three alkyl groups causes a considerable increase in IP_R. Hence, in the latter case stabilization of the excited state takes place. Naturally, for the higher Rydberg states this effect becomes weaker.

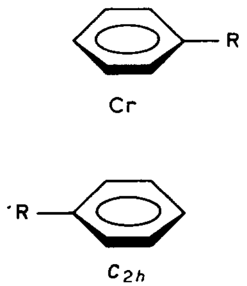
The system C in the vapour spectra corresponds to the intense band in the solution spectra which is assigned to an allowed electrodipole component of the $e_{2g} \rightarrow e_{2u}^{\star}$ transition ($^1A_{1g} \rightarrow {}^1A_{2u}$) for $(C_6H_6)_2Cr^0$ based on the SCF MS X_α calculation [9]. Berry [1] assigned system C to an allowed component of $e_{2g} \rightarrow e_{1u}^{\star}$ ($^1A_{1g} \rightarrow {}^1E_{1u}$). It is quite possible that both transitions make a contribution to the system. Diffuse character of the C system bands in the spectrum of I [1] may be indicative of instability in the excited state with respect to dissociation, furthermore, it can be due to the corresponding transition including the electrons from the bonding MO, such as e_{2g} [10]. The frequencies of the system C bands are listed in Table 2.

System B in the spectrum of I has a distinct vibrational structure. A large relative intensity of the main band (Fig. 1) as well as the presence of a hot band, a totally symmetric vibration frequency away from the main band [1] which indicates that the corresponding electronic transition is allowed as one of an electrodipole. There is a progression of neighbouring bands which are 240–270 cm^{-1} apart. This value which corresponds to the totally symmetric vibration frequency for the excited state of the complex is equal to the frequency of the a_{1g} ring-vibrational modes in relation to the central chromium atom for $(C_6H_6)_2Cr^0$ in the ground electronic state (270 cm^{-1} from the Raman spectrum [11]). So it can be assumed that a transition of an electron from the non-bonding orbital takes place. Berry [1] assigned system B to a symmetry-allowed component of $e_{1u} \rightarrow e_{1g}^{\star}$ ($^1A_{1g} \rightarrow {}^1A_{2u}$). However, this assignment seems to be unlikely. From photoelectron spectroscopy data [4], $IP_{e_{1u}}$ for I is about 9.6 eV, 4.2 eV greater than $IP_{a_{1g}}$. Consequently, a rough estimate gives the energy of the $e_{1u} \rightarrow e_{1g}^{\star}$ transition as being 4.2 eV (33900 cm^{-1}) greater than that of the $a_{1g} \rightarrow e_{1g}^{\star}$ transition. Thus the $e_{1u} \rightarrow e_{1g}^{\star}$ band should be observed at considerably shorter wavelengths than those of system B, and in accordance with the calculation [9] the corresponding frequency is 52750 cm^{-1}. Assignment of B to a transition from the highest occupied MO a_{1g} to one of the lowest vacant a_{2u} or e_{1u} orbitals seems more plausible. It is possible that this is a Rydberg transition.

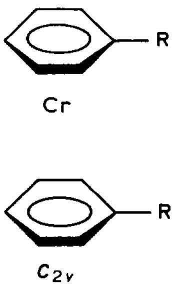
The strongest band of system B in spectrum I is tentatively assigned to the O–O-transition. The fourth band of the progression (27470 cm^{-1}) is separated by 770 cm^{-1} from the strongest band. This value corresponds to the totally symmetric C–H bending frequency (790 cm^{-1} in $(C_6H_6)_2CrI$ [12]). That is obviously why the fourth band is stronger than the third one (Fig. 1).

In the comparison with the O–O-band of I, the strong bands of system B in the spectra of II–VI undergo red-shift. The B structure remains practically unchanged on passing from I to II and III, though the bands in spectra II and III become blurred. However, the system changes markedly on passing from I to IV and V (Fig. 1). This fact makes it difficult to find similarities between the absorption bands of IV, V and those of I. System B for bis(mesitylene)chromium(0) has no vibrational structure. In contrast with $IP_{a_{1g}}$, the strong band frequencies of II–VI are changed nonmonotonically. First their shift from the O–O-band of I increases, but then it becomes smaller. The shifts for II and VI are almost equal. It can take place if introduction of alkyl substituents into the benzene rings results in a shift of the minimum on the potential energy surface for the excited state, with respect to that for the ground state. Thus the molecular equilibrium configurations for the substituted complexes in the ground and excited electronic states are different. In that case the strong bands of IV–VI do not correspond to the O–O-transition. The change in structure of system B may be caused by a splitting of the degenerated excited state level when molecular symmetry is reduced.

Most of the weak longwave bands of the investigated spectra are part of system A. From the absorption spectrum I we could not determine whether these bands should be assigned to the symmetry forbidden electrodipole transitions where the inactivity is partially obscured by vibronic interaction, or to the spin-forbidden transitions. The relative intensity of the A bands with respect to B in the spectra of II–V is significantly larger than that in the spectrum of I (Fig. 1). This may have been caused by a reduction in the molecular symmetry. The most symmetric configuration of complexes II–V is C_{2h} or C_{2v}:



C_{2h}



C_{2v}

The C_{2h} configuration is more advantageous because of reduced repulsion by the substituents. When the symmetry is reduced from D_{6h} to C_{2h}, all the $g \leftrightarrow u$ transitions become allowed. So, the $a_{1g} \rightarrow e_{2u}^{\star}$ transition ($^1A_{1g} \rightarrow {}^1E_{2u}$) which is forbidden in the D_{6h} group, becomes allowed when the symmetry is reduced to C_{2h}. This transition is longwave in the $(C_6H_6)_2Cr^0$ spectrum, because a_{1g} is the highest occupied MO and $e_{2u}^{\star}$ is one of the lowest unoccupied orbitals [9]. The A bands in the spectra of II–VI are assigned to this transition. However, it is difficult to establish which band in system A of the spectrum of I corresponds to the $a_{1g} \rightarrow e_{2u}^{\star}$ transition.

In accordance with the photoelectron spectroscopy data [4,5] the difference between $IP_{e_{2g}}$ and $IP_{a_{1g}}$ is about 1 eV for $(C_6H_6)_2Cr^0$. If the electronic transition energy is regarded generally as a difference between MO energies, then the energies of the transitions from a_{1g} and e_{2g} into the same vacant orbital must differ by about 8000 cm^{-1}. This value is consistent with the observed difference between the band frequencies of the systems C and A, and confirms the assignment of A suggested by us. However, there is another possibility viz. the assignment of system A to the Rydberg transition which, although it'is forbidden in the D_{6h} point group, it is allowed when the symmetry is reduced.

The effect of alkyl substituents on the bis(arene)chromium(0) absorption spectra shows that the introduction of a methyl or ethyl group into each ring does not cause a significant change in band structure. For complexes IV–VI, however, the shape of the bands is changed to some extent. For VI the perturbation of the bis(benzene)chromium(0) MO by the introduction of alkyl substituents is obviously sufficient to exert a significant influence on the shape of the absorption spectrum.

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