

## Remarks on the Electronic Spectra and Structures of Compounds of Chromium and Benzene\*

R. STEPHEN BERRY

*Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut*

(Received December 19, 1960)

An orbital level diagram and assignments of electronic spectra are given for the benzene-chromium compounds. These are based principally on symmetry arguments, atomic spectra and dichroism measurements. The problem of the energy involved in distorting benzene rings is also discussed.

### I. INTRODUCTION

THIS note is written in an attempt to interpret the electronic spectra<sup>1,2</sup> and skeletal structure<sup>3</sup> of the benzene-chromium compounds and to relate these to a set of orbitals based on molecular symmetry and spectral assignments. We shall discuss the assignments particularly in terms of polarization, and also of intensity; we shall then consider aspects of the energetics of the distortion of the benzene ring. No attempt is made to carry out extensive orbital calculations; rather, we can compare our empirically deduced orbital diagram with those calculated for the cyclopentadienyl-metal compounds like ferrocene.<sup>4-6</sup>

Crystalline dibenzene chromium itself is composed of two distorted benzene rings which can be pictured easily as lying on opposite threefold faces of an octahedron about the chromium atom. The observed C—C bond distances,<sup>3</sup> 1.353 and 1.439 Å, correspond closely to a hypothetical cyclohexatriene molecule. The short C—C bonds of one ring lie opposite the long bonds of the other, giving the molecule  $D_{3d}$  symmetry. It is perhaps easiest to interpret the behavior of this molecule and the other arene-chromium compounds by starting with the picture of two benzene rings in  $D_{6h}$  symmetry (one directly above the other), lying on opposite faces of a chromium atom in a  $d^6$  configuration, or more specifically, in a pseudo-octahedral field. Then the six electrons of chromium fill the  $t_{2g}$  orbitals. These orbitals point toward alternate C—C bonds in just the way necessary to force the ring  $\pi$  electrons into the  $D_{3d}$  structure. (This approach has the convenience that  $D_{3d}$  is a subgroup of both  $D_{6h}$  and  $O_h$  although neither of these two is contained in the other.) The now-

trigonal structure of the two benzene rings lowers the symmetry of the ligand field about the chromium, causing the  $t_{2g}$  level to split into  $a_{1g}$  and  $e_g$  orbitals. The  $3d a_{1g}$ , in a natural coordinate system for the trigonal field, looks like  $2z^2 - x^2 - y^2$ , with a density maximum pointing toward the center of the rings. This  $a_{1g}$  orbital can mix with the  $4s a_{1g}$  orbital which looks like  $x^2 + y^2 + z^2$ , to produce a low-energy  $a_{1g}$  level with high density midway between the rings, and a high-energy orbital pointing its density very strongly toward the benzene rings. The  $e_g$  orbitals from the octahedral  $t_{2g}$  set, and the higher  $3d e'_g$  orbitals can also mix, so that the low-energy  $e_g$  pair have nodal surfaces principally cutting the octahedral faces where the rings lie, while the other, high-energy  $e'_g$  orbitals have their nodal surfaces mainly out of the way of the benzene rings. We shall also have to consider the  $4p a_{2u}$  and  $4p e_u$  orbitals in the trigonal field. Figure 1 indicates the relation of the  $D_{3d}$  cyclohexatriene structure to the octahedral ligand field.

In the benzene-chromium compounds, the empty  $3de'_g$  orbitals have particularly high amplitudes close to the short C—C bonds. It is reasonable to expect that a large fraction of the binding energy involving the  $\pi$  electrons occurs as a result of mixing the  $\pi e_g$  orbitals with these  $3d e'_g$  orbitals. The only other orbital mixing which will be particularly important to us is that of the  $4p e'_u$  chromium orbitals and the excited ring  $\pi e'_u$  orbitals.

### II. SPECTRA AND ORBITAL LEVELS

With the foregoing introduction as a basis, we can use the observed spectra of the complexes,<sup>1,2</sup> the ionization potentials of benzene<sup>7</sup> and chromium,<sup>8</sup> and the atomic spectrum of chromium<sup>8</sup> to infer the orbital structure of the benzene-chromium compounds, and to assign their spectral band systems. In their discussion of spectra, Yamada *et al.*<sup>1,2</sup> report six bands, as indicated in Table I. They suggest that Band IV is due to a  $\pi \rightarrow \pi^*$  transition within the rings, on the basis of in-

<sup>7</sup> W. C. Price and R. W. Wood, *J. Chem. Phys.* **3**, 439 (1935); K. Watanabe, *ibid.* **22**, 1564 (1954).

<sup>8</sup> Charlotte E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. II.

\* Contribution Number 1649 from the Sterling Chemistry Laboratory, Yale University.

<sup>1</sup> S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan* **30**, 647 (1957).

<sup>2</sup> S. Yamada, H. Yamazaki, H. Nishikawa, and R. Tsuchida, *Bull. Chem. Soc. Japan* **33**, 481 (1960).

<sup>3</sup> F. Jellinek, *Nature* **187**, 871 (1960).

<sup>4</sup> These calculations have been reviewed in detail by (a) G. Wilkinson and F. A. Cotton, *Prog. Inorg. Chem.* **1**, 1 (1959). See especially (b) J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.* **23**, 954 (1955) and references 5 and 6.

<sup>5</sup> M. Yamazaki, *J. Chem. Phys.* **24**, 1260 (1956).

<sup>6</sup> A. D. Liehr and C. J. Ballhausen, *Acta Chem. Scand.* **11**, 207 (1957).

TABLE I. Representative spectral information.\*

Compound	Form	Band I'	"Spin-forbidden" band	Band I	Band II	Band III	Band IV
$b_{2g}CrI$	H <sub>2</sub> O soln. frequency (ev)	1.07	2.15	3.14	3.72	4.57	5.51
	log $\epsilon_{max}$	0.95	1.8	approx 2.75	3.76	3.75	4.14
	Ethanol soln. frequency			approx 3.14	3.71	4.54	5.75
	log $\epsilon_{max}$			approx 2.75	3.80	3.78	4.28
	Crystal frequency			2.77	3.55-3.72	4.36	>4.96
	log $\alpha_{max}$			1.85	1.75	1.7	"marked"
	(stronger component)						
	Polarization			<i>x, y, z</i>	<i>x, y, z</i>	<i>z</i>	<i>x, y</i>
	(stronger component boldface)						
$b_{2g}Cr(CO)_3$	Methanol soln. frequency	(absent)	2.19-2.23	3.30	3.98	4.89	
	log $\epsilon_{max}$		1.8	3.3	3.86	3.74	
	Ethanol soln. frequency	(absent)	2.27-2.31	3.30	3.97	4.88	
	log $\epsilon_{max}$		1.8	3.4	3.54	3.64	
	Crystal frequency			3.26	4.01		
	log $\alpha$			1.85	1.9		
	(stronger component)						
	Polarization			<i>x, y, z</i>	<i>x, y, z</i>		

\* See references 1 and 2.

ensity, polarization and solvent shift. They also point out that the frequency of this band is not characteristic of a benzenoid transition and suggest that when the benzene-chromium compounds form, considerable change in the aromatic system takes place. We accept their assignment of Band IV, and can add a little theoretical evidence which perhaps helps to support their identification. The two extreme models which one can choose for the  $\pi$  electrons of the benzene rings are (a) the usual molecular orbital model in which the six  $\pi$  electrons are completely delocalized and move in an uncorrelated way over the entire ring, and (b) a localized double-bond model in which the  $\pi$  electrons are restricted to staying in their own electron-pair bonds. The former can be improved in the usual way with the help of configuration interaction. The latter can be improved in two steps; ultimately, we might include many valence bond structures and obtain the same result that we would get from the MO picture; along the way, however, we might keep the double bonds localized and yet permit them to interact via dispersion forces. These do seem to be the major source of interaction between  $\pi$  electron pairs in the polyenes.<sup>9,10</sup> In either an MO or interacting-double-bond model, the first allowed transition of benzene is  ${}^1E_{1u} \leftarrow {}^1A_{1g}$ , which appears at about 7.3 ev in benzene. The interacting-double-bond model places this transition at considerably lower energy; we can see this as follows. We construct wave functions based on the two-electron functions for three individual double

bonds,  $A$ ,  $B$ , and  $C$ , so that the ground-state  $\Psi_0$  may be written as a product  $ABC$ . Then the first excited state is one in which all three electron pairs share excited character (the exciton model). This can be written as

$$\Psi_{\pm} \sim ABC^* + \exp(\pm 2\pi i/3) AB^*C + \exp(\pm 4\pi i/3) A^*BC.$$

The excitation energy can be expressed as

$$\Delta E = (A/\mathfrak{C}/A^*) - (AB^*/\mathfrak{C}/A^*B).$$

The parameters  $(A/\mathfrak{C}/A^*)$  and  $(AB^*/\mathfrak{C}/A^*B)$  might be found empirically from the spectra of ethylene and *cis*-butadiene, respectively. The former is known to be 7.6 ev. The *cis*-butadiene spectrum has not been reported; we take the value of 1.8 ev on the basis of a calculation carried out for both *cis*- and *trans*-butadiene<sup>11</sup> which gives good agreement for the uv spectrum of the *trans*-molecule. Hence the model predicts the  $\pi \rightarrow \pi^*$  transition to fall at 5.8 ev, which may be compared with the observed value of 5.51 and 5.75 ev for dibenzene chromium iodide in water and ethanol solutions, respectively. (We might point out that the observed benzene levels  ${}^1B_{2u} < ({}^1B_{1u}?) < {}^1E_{1u}$  are quite different in the exciton model, which gives  ${}^1E_{1u} < {}^1B_{2u} < {}^1B_{1u}$ .) We take this "agreement" to indicate that the assignment of Band IV as a  $\pi \rightarrow \pi^*$  transition is reasonable, and that the interaction between the ring and chromium electrons may introduce some localization of the  $\pi$  electrons which in turn causes the frequency of the benzene  ${}^1E_{1u} \leftarrow {}^1A_{1g}$  transition to drop. With this assignment made, we may proceed to the other bands.

<sup>9</sup> W. T. Simpson, J. Am. Chem. Soc. **73**, 5363 (1951); **77**, 6164 (1955).

<sup>10</sup> R. S. Berry, J. Chem. Phys. **30**, 936 (1959).

<sup>11</sup> R. S. Berry, J. Chem. Phys. **26**, 1660 (1957).

We can start to place orbitals on an energy scale and to assign transitions. Figure 2 shows the levels and transitions as we shall now derive them. The  $\pi \rightarrow \pi^*$  transition is presumably that involving the  $\pi e_u$  filled and  $\pi e_g'$  unfilled levels, neither of which is appreciably shifted from its hypothetical unperturbed origin by any nearby metal orbital. The  $\pi a_{1g}$ ,  $\pi a_{2u}$ ,  $\pi a_{1u}'$ , and  $\pi a_{2g}'$  orbitals can be placed approximately if we do a straightforward semiempirical molecular orbital calculation, using the observed 5.75-ev energy difference as the characteristic parameter ( $\beta' + \beta''$ ). (There are two interaction integrals rather than  $\beta$  alone, but the form of the energy levels is the same as that of benzene, if one replaces  $2\beta$  with  $\beta' + \beta''$ .)

Band III is the only band whose dichroism shows a minimum in its less intense component at the same frequency its stronger  $z$ -polarized component has a maximum.<sup>1</sup> This we take to indicate that there is little or no  $x$ ,  $y$ -polarized contribution to Band III. It must therefore be an  $a_{1g} \rightarrow a_{2u}$  transition, and can be either  $\pi a_{2u} \rightarrow d a_{1g}'$  or  $d a_{1g} \rightarrow \pi a_{2u}'$ . The excited  $a_g'$  metal orbital is necessarily higher after interacting with the lower-energy filled  $a_{1g}$  chromium orbital, and must therefore be more than 5 ev above the  $\pi a_{2u}$  level. It is probably higher still. The assignment of Band III is therefore made as  $a_{1g} \rightarrow a_{2u}'$ , involving orbitals principally associated with the metal atom.

The next band we assign is I', a band appearing only in the  $\text{Cr}^+$  compounds. It seems very probable that this involves a transition to a hole in the  $e_g$  or  $a_{1g}$  orbital, whichever is higher. On the basis of intensity, the transition seems to be forbidden, and, therefore, Yamada *et al.* have suggested that it involves metal orbitals alone. Guided by atomic energy levels, the orbital calculations for ferrocene,<sup>4-6</sup> and the assignment of Band I as described below, we choose to place  $a_{1g}$  below  $e_g$ , and to assign I' as a transition  $a_{1g}^2 e_g^3 \rightarrow a_{1g} e_g^4$ , which does involve metal orbitals principally, and is symmetry forbidden. No possibility exists for any intraconfigurational transitions involving  $a_{1g}^2 e_g^3$  or  $a_{1g} e_g^4$ . The chromium (I) compounds do have the possibility of exhibiting an allowed  $\pi e_u \leftrightarrow e_g$  transition.

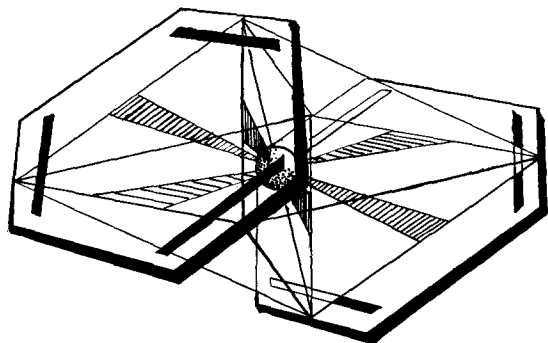


FIG. 1. Benzene rings on threefold-symmetric faces of an octahedron. The directions of six of the electron-density maxima for  $t_{2g}$  orbitals are shaded, to indicate how the repulsion of  $\pi$  and  $d$  electrons might introduce a distortion of the benzene rings.

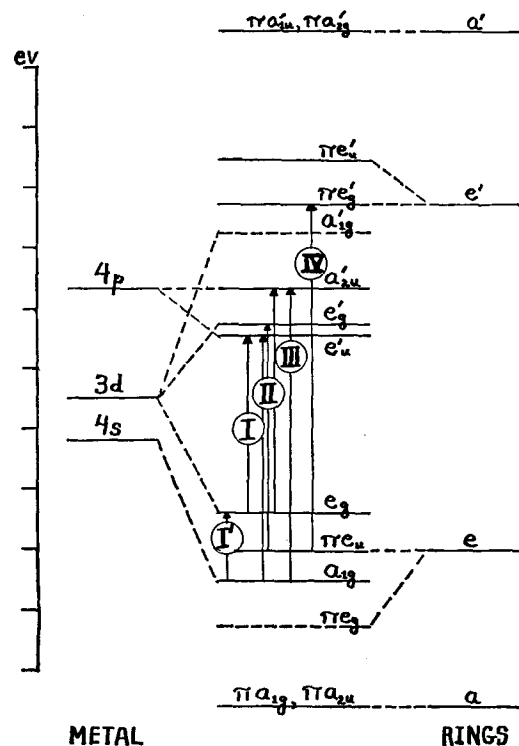


FIG. 2. Orbital diagram and spectral assignments. Energies are chosen to fit dibenzene chromium iodide in ethanol, according to the data of reference 1, but the other compounds are essentially the same.

Presumably this falls at still lower energy than the weak Band I'. We therefore place the  $e_g$  orbitals approximately 1 ev above the  $a_{1g}$ , to agree with our assignment of Band I', and put the  $\pi e_u$  level midway between these two, to account for the nonobservance of the long wavelength allowed electronic transition.

To help us place the other orbitals and assign the other bands, we examine the orbital energy levels of the separated rings and chromium atom. Let us assume that the ionization potential of a "cyclohexatriene" ring is the same as that of benzene, namely, 9.24 ev.<sup>7</sup> The ionization potential of  $\text{Cr}^0$  is 6.763 ev<sup>8</sup> so that we can place the unsplit  $3d$  orbitals of Cr approximately 2.5 ev above the  $\pi e_u$  orbitals of the ring system. From observed atomic energies,<sup>8</sup> we can estimate that the chromium  $4s$  level lies 0.65 ev below the  $3d$ , and the  $4p$  level, 2.5 ev above the  $4s$ . Then in formation of dibenzene chromium, the  $4s$  and  $3d$  levels split into upper and lower groups, each containing an  $a_{1g}$  and an  $e_g$  set, as shown in Fig. 2.

The  $4p$   $a_{2u}$  level finds no nearby orbital of similar symmetry and therefore is not shifted, in first order. This fits well (within 0.3 ev) with the placement and assignment of Band III. The other  $4p$  orbitals of symmetry  $e_u$ , can mix with the empty  $\pi e_u'$  orbitals to give one doubly degenerate set below the  $4p$  atomic limit and another pushed above the  $\pi e_g'$  level. With this qualitative arrangement, we find that four allowed transitions should appear with energies between 3 and 4 ev.

One of these transitions is in principle fixed by the previous assignments of I' and III. These two imply that the  $e_g \rightarrow a_{2u}'$  transition should fall at about 3.5 eV, which suggests that it is part of Band II. We can probably reject its assignment to Band I because of the low intensity of the latter, but even without the intensity problem, we would find this difficulty: If the  $e_g \rightarrow a_{2u}'$  transition were part of I, and if  $a_{1g}$  is about 1 eV below  $e_g$ , then  $e_u'$  is about 1 eV below  $a_{2u}'$ , so that the allowed transition  $e_g \rightarrow e_u'$  should fall approximately 1 eV below I. But no transition is observed in the 2-eV region of the spectrum, so we presume that  $e_g \rightarrow a_{2u}'$  and similarly  $a_{1g} \rightarrow e_u'$  both contribute to II. These are both pure  $x, y$ -polarized bands.

The placement of the two  $a_g \rightarrow e_u$  transitions immediately tells us that the allowed  $e_g \rightarrow e_u'$  band can be assigned as transition I, and the remaining charge transfer process  $\pi e_u \rightarrow e_g'$  as that part of II which contributes its  $z$  component of polarization. Without this, there would be no such component in our analysis. Hence the  $e_g'$  level lies about 1.2 eV above the unsplit  $3d$  level, as drawn in the figure.

An alternative explanation for the first three bands might identify Band I as involving the excited  $a_{1g}'$  orbital, which falls quite low in the calculations of Yamazaki<sup>6</sup> for ferrocene. This would require, however, that the  $e_g'$  orbitals also lie at low energies and that  $a_{1g}$  and  $e_g$  be nearly degenerate, in order to account for the  $x, y$ -polarized component of the transition. This, in turn, would require that either  $\pi e_u \rightarrow e_g'$  allowed transition be found at comparable energy, or that the  $a_{1g}$  and  $e_g$  chromium be somewhat above the  $\pi e_u$  level. This, in turn, would imply the existence of a strong band for Cr (I) at about 1 eV, which is not observed. Regarding the position of the  $a_{1g}'$  orbital, it is very possible that it lies higher than shown in the diagram, to maintain the center of gravity of the levels.

Regarding the "spin-forbidden" transition, it is tempting to assign this as arising from the same configuration as one of those produced by transition I or II since these would make the transition allowed on all grounds except spin. On the basis of our orbital diagram, there is no singlet-singlet Laporte-forbidden transition within the  $4s-3d$  shell which could fit. Furthermore, an oscillator strength of no more than  $10^{-5}$ , estimated from the data of reference 2, is consistent with this assignment.

We might briefly consider intensities in the other bands. For Band I',  $f$  seems to be of the order of  $10^{-3}$ , consistent with its assignment as a symmetry-forbidden spin-allowed transition. In solution, Bands I, II and III have estimated oscillator strengths of about 0.01, 0.1 and 0.1, respectively. The solution spectra give an intensity for Band I which seems quite low for the assignment we have made. The crystal spectra intensities are somewhat higher, consistent with our assignment. It is quite possible that the rings become regular hexagons in solution, according to the infrared

and Raman spectra.<sup>12,13</sup> Then the molecule goes into  $D_{6h}$  symmetry. In the  $D_{3d}$  symmetry of the crystal, the transition of Band I gives excited states of  $A_{1u}, A_{2u}$  and  $E_u$  symmetry; the  $A_{2u}$  is achieved by an allowed  $z$ -polarized transition and the  $E_u$ , by allowed  $x, y$ -polarized transition. In  $D_{6h}$  symmetry, the upper states can be  $B_{1u}, B_{2u}$  and  $E_{1u}$ ; only the latter is allowed, and that by  $x, y$ -polarized radiation only. The dichroism measurements show that the  $x, y$  component of Band I is indeed weaker than the  $z$  component in the crystal spectrum, as one would expect if the  $e_u'$  orbitals contain a large contribution from the  $\pi e_u'$  ring orbitals. In effect, the stronger component has considerable charge-transfer character. This component becomes forbidden if the symmetry becomes  $D_{6h}$ , and will decrease markedly in intensity if the rings approach hexagonal symmetry closely. By contrast, when  $D_{6h}$  symmetry is achieved, Band II loses the  $x, y$ -polarized part of the  $\pi e_u \rightarrow e_g'$  transition and the entire ( $x, y$ -polarized)  $e_g \rightarrow a_{2u}'$  transition, but keeps the  $a_{1g} \rightarrow e_u'$   $x, y$ -polarized transition and especially the  $z$ -polarized component of the  $\pi e_u \rightarrow e_g'$  transition, which is probably the strongest part of Band II. Band III retains its allowed character also, if the rings become regular.

With regard to solvent shifts, we can say relatively little except to speculate that perhaps solvents interact as follows. Interaction is negligible with the "protected"  $4p$   $a_{2u}$  orbital, and slight with the  $a_{1g}$  occupied chromium orbital, so that III shows a blue shift. Interaction energies between solvent and orbitals  $e_g$  and  $e_u'$  may be about the same, so that there is no blue shift observed for I. This suggests that the blue shift of II is due at least in part to its  $e_g \rightarrow a_{2u}'$  contribution. One might expect that the  $e_g'$  orbitals would be protected and suffer little interaction with solvent, so that the  $\pi e_u \rightarrow e_g'$  component could also contribute to the blue shift of II.

Comparing our orbital diagram with those derived from various approaches for ferrocene,<sup>4-6</sup> we find a rough similarity to all that these results, (which almost necessarily arises from the order of the levels of the separated systems). Our diagram is particularly close to the results of Dunitz and Orgel.<sup>4</sup> They have not inquired into the splitting of the  $4p$  levels, so that their  $4p$  level lies above the  $e_{1g}'$ , analogous to our  $e_g'$ ; this is in accord with our unshifted  $a_{2u}'$ , but we have placed the  $e_u'$  level below  $e_g'$ . We have reversed their order of the filled  $3d$   $a_{1g}$  and  $e_g$  orbitals, in order to account for the  $z$  component of the polarization of Band I. But in the dibenzene chromium system, this orbital can interact with the other  $3d$   $e_g$  level, while in ferrocene, the two sets are of different symmetries ( $e_{2g}$  and  $e_{1g}$ , respectively) and cannot interact. We also have placed the  $\pi e_1$  filled orbital between the  $e_g$  and  $a_{1g}$  filled levels. The details of the order of these three closely spaced

<sup>12</sup> H. P. Fritz, W. Lüttke, H. Stammreich, and R. Forneris, Chem. Ber. **92**, 3246 (1959).

<sup>13</sup> R. G. Snyder, Spectrochim. Acta **15**, 807 (1959).

levels might be verified by a study of the dichroism of Band I'. The calculations of Dunitz and Orgel place the unfilled  $a_{1g}'$  level rather high, at about the same energy as the unfilled  $e'_{1g}$  level of ferrocene. As we pointed out previously, the  $a_{1g}'$  chromium level might perfectly well be placed at about the same energy as the  $e_g'$ . The level scheme of Yamazaki<sup>5</sup> is essentially similar, so far as the filled levels go, except that it places the ring  $e_u$  level above the metal  $e_g$  level. The unfilled orbitals of this calculation, which are apparently consistent with the first two observed bands of ferrocene, are much more closely spaced, than those of Fig. 2, especially because Yamazaki places the  $3d$   $a_{1g}$  and  $4p$   $a_{1u}$  levels below the unfilled  $e$  levels. If this were the case of the benzene-chromium compounds, then these would be pure  $x$ ,  $y$ -polarized bands in the region below 3 ev, and no such bands have been observed. Liehr and Ballhausen<sup>6</sup> have placed the metal  $a_{1g}$  and  $e_g$  filled orbitals together for bicyclopentadienyl chromium. Such a degeneracy fits nicely with our notion that the  $t_{2g}^6$  configuration is a good starting approximation in the benzene-chromium compounds. Nonetheless our assignment of Band I' implies that there should be some separation of these two levels when benzene is a ligand. Their electrostatic model places the unfilled  $a_{1g}'$  orbital below the  $e_{1g}$  pair, in contrast to Fig. 2; it also places the  $4p$   $e_u$  level below the  $4p$   $a_u$ , as our interpretation does, in contrast to the results of Yamazaki.

A recent treatment by Robertson and McConnell<sup>14</sup> of magnetic resonance properties of sandwich compounds suggests that perhaps the  $e_g$  metal orbital lies below the  $a_{1g}$ . This suggestion is based on the fact that the observed  $g$  value of dibenzene chromium (I) is close to the free electron value. It is quite possible that this might be the case. This would require the assignment of Band I as a  $\pi e_u \rightarrow e_g'$  process with considerable charge-transfer character, implying that it should be rather intense. This would also require that the  $4p$   $e_u$  level be raised about 1 ev so that the  $a_{1g} \rightarrow e_u'$  transition fall with II, rather than I. But this leaves no  $e_g \leftrightarrow e_u$  transition to provide the  $z$  polarized component of Band II, and would also shift the  $4p$  level higher and the  $3d$  level considerably lower. We therefore prefer to assume for the time being that the  $e_g$  level is higher than the  $a_{1g}$ , and that the orbital angular momentum is nearly quenched, making the  $g$  value near 2. This might be connected either with the large spin density appearing on the rings<sup>15</sup> or with the detailed way in which the two sets of  $e_g$  orbitals derive from atomic  $d$  orbitals, or both.

We may conclude with a few miscellaneous comments about the spectra of the benzene-chromium compounds. The fact that benzene chromium tricarbonyl<sup>2</sup> shows no  $z$ -polarized Band III is in no way a difficulty. The lowest  $\pi-\pi^*$   $x$ ,  $y$ -polarized transition of

the three carbonyl groups could easily be responsible for the rising  $x$ ,  $y$  component of the crystal spectrum around 2700 Å, where the data end. The spectrum of dibenzene chromium (0) itself has not been reported. We can predict rather easily that it should have a spectrum much like dibenzene chromium iodide, except that Band I' will be missing. Furthermore, someplace beyond Band IV, there should be more bands of the metal-to-ring type, and probably at quite high energies, another  $\pi \rightarrow \pi^*$  transition like the allowed transition of Band IV, but involving  $\pi e_g$  and  $\pi e_u'$ . It is possible that this band may lie in the 1700–1800 Å region; as our diagram is drawn, however, we would place it closer to 1400 Å.

### III. RING DISTORTION

The next matter we wish to discuss is the problem of the energy involved in distorting the benzene rings into the structures observed in the dibenzene chromium crystal.

One model which we can use is based on the stable benzene ring as a starting point. We can use the appropriate force constant data taken from the infrared spectrum of benzene to estimate the increase in total ring energy when alternate C—C bonds are stretched and compressed to give the distorted structure. We can also estimate how much of this is pure  $\pi$  electron energy from a semi-empirical molecular orbital model. The appropriate motion of the carbon atoms is almost exactly (to within about 0.001 Å) a motion along the C—C stretching symmetry coordinate of symmetry type  $B_{2u}$ ,

$$S_{14} = (1/6^{\frac{1}{2}}) (r_1 - r_2 + r_3 - r_4 + r_5 - r_6),$$

where  $r_1$  through  $r_6$  represent the six bond lengths. The frequencies of the  $B_{2u}$  vibrations were found by Mair and Hornig<sup>16</sup> to be 1311 and 1147  $\text{cm}^{-1}$  and the carbon-carbon force constant for  $S_{14}$  was obtained by Hornig<sup>17</sup> as either 4.361 or  $3.926 \times 10^5/\text{cm}$ . From these values, we find that the ring structure observed in dibenzene chromium lies only 3.48 or 3.13 kcal away from the potential minimum. The zero-point energy of the  $B_{2u}$  higher-frequency vibration is 1.87 kcal. Therefore a benzene ring needs only 1.61 or 1.26 kcal to arrive at the distorted form adiabatically. Alternatively, since the first overtone of the 1311  $\text{cm}^{-1}$   $B_{2u}$  vibration shows that the potential curve is very harmonic,<sup>17</sup> we can use the harmonic oscillator function to find that the observed distorted structure lies 1.36 or 1.29 classical amplitudes from the potential minimum, and therefore, if other motions are neglected, an ordinary free benzene ring in its ground vibrational state spends between 33.4 and 36% of its time at least as distorted as the rings found in dibenzene chromium crystal. In order for the rings to show stable vibrations in the crystal, at frequencies comparable to the free benzene frequencies<sup>12, 13</sup>

<sup>14</sup> R. E. Robertson and H. M. McConnell, J. Phys. Chem. **64**, 70 (1960).

<sup>15</sup> R. O. Feltham, P. Sogo, and M. Calvin, J. Chem. Phys. **26**, 1354 (1957).

<sup>16</sup> R. D. Mair and D. F. Hornig, J. Chem. Phys. **17**, 1236 (1949).

<sup>17</sup> D. F. Hornig, J. Am. Chem. Soc. **72**, 5772 (1950).

the potential minimum of the distorted configuration (in the presence of a chromium atom, of course) must be at least as far below the energy of the regular form as the energy of the free distorted molecule lies above that of the free regular hexagon. If we assume that the undetected  $B_{2u}$  mode ( $\nu_{14}$ ) of the rings in dibenzene chromium has its frequency shifted as little as the observed modes,<sup>12,13</sup> then we can infer that the distorted structure needs about 6.5 kcal or more, per benzene, to stabilize it. It would be very helpful if this mode could be detected somehow. Conceivably,  $\nu_{14}$  might be at considerably lower energy in dibenzene chromium than in benzene itself.

Before we continue this line of reasoning, let us try to estimate the change in energy of the  $\pi$  electrons alone in our delocalized-electron model, when the benzene skeleton is distorted. We use two values,  $\beta'$  and  $\beta''$ , for the interactions across long and short double bonds, respectively.<sup>18</sup> The orbital level scheme is the same as for benzene except that  $\beta$  must be replaced by the average of  $\beta'$  and  $\beta''$ . We can examine  $(\beta' + \beta'')/2\beta$  with the help of the formula given by Mulliken<sup>19</sup> for variation of  $\beta$  under small displacements,

$$\beta/\beta' = [S/(1+S)] \cdot [(1+S')/S'].$$

The  $p\pi$  overlap integrals are 0.242 for the benzene distance, and 0.278 and 0.233 for the observed ring distances (with  $Z=3.18$  in the  $2p\pi$  functions). Then the ratio  $(\beta' + \beta'')/2\beta$  is 1.046. Therefore, according to the "magic formula," we would conclude that the  $\pi$  electron system of benzene is more stable with a three-fold-symmetric skeleton than with a regular hexagon. This is perhaps an example of the limitation of the formula. In any case, it would appear from this calculation, just as with a conjugated polyene, like butadiene, that the change of  $\pi$  electron energy associated with small distortions of the skeleton is itself small. By "small," we mean only that the energy is small compared with the total  $\pi$  electron interaction energy, or with the energy necessary to establish a harmonic potential well supporting, say three or more levels. The energy is not small compared with the zero-point energy and can definitely influence the force constants of bonds. The  $B_{2u}$  benzene skeletal vibration frequency, for example, has a zero-point energy very close to our estimate of the  $\pi$  electron energy change.

In view of the rather low energy necessary to displace the potential minimum, and of the direction which the  $\pi$  electron energy change might have, we are led to suggest that perhaps the rings of dibenzene chromium are distorted in the crystal and are regular hexagons in fluid phases. The frequency of the  $B_{2u}$

vibration of dibenzene chromium becomes a very important quantity, since it is a measure of the ease with which this distortion can be made. Crystalline benzene itself shows anisotropic motion of the carbon atoms,<sup>20</sup> in which the amplitudes are particularly large along the circumscribed circle about the regular hexagon. This motion has been attributed to libration. The distorted structure of benzene in dibenzene chromium leaves the carbon atoms on this circle circumscribed about the regular hexagon. Perhaps part of the apparent anisotropic motion of benzene is due to the  $\beta_{2u}$  ( $\nu_{14}$ ) normal mode, with its rather large amplitudes.

Up to this point we have not discussed the difference in the energy associated with localizing the  $\pi$  electrons of benzene. We have only showed that in benzene itself, the distortion involves a rather small total energy change which might be opposite in direction to the change in pure  $\pi$  electron energy. The phenomenon we may ask about now is this: when a benzene ring is distorted, to what extent do electron correlations lead to increased contributions from pairwise-localized canonical structures in the exact wave function? We must specify "pairwise-localized" structures rather than just Kekule's structures because it is important to include dipole-dipole correlations in assessing the behavior of neighboring double bonds.<sup>9,10</sup> Then, we can ask what effect the presence of perturbing charges like the  $d$  electrons of chromium will have on the  $\pi$  electron wave function of benzene. We shall not try to answer these questions at this time, except to make a cursory comparison on the basis of the observed spectra. For benzene, the center of gravity of the three lowest singlet states lies at 6.0 eV, which we may take as twice the separation of the lowest unfilled and highest filled orbitals. The spectrum of butadiene and the estimate made in Part II of this paper suggest that the energy difference between highest filled and lowest unfilled orbitals of "cyclohexatriene" is about the same as for ethylene. (The spectral shift is attributed to the splitting of terms within a configuration.) This value is 7.6 eV. A cyclohexatriene orbital model in its crudest form makes all three filled orbitals degenerate; this is the form on which our dispersion interaction is based. Then the energy of the cyclohexatriene  $\pi$  electron system is of the order of  $6 \times 7.6/2$  or 22.8 eV. The benzene  $\pi$  electron energy is  $2 \times 2 \times 3 + 4 \times 3$  or 24 eV, and the net difference in energy of the two  $\pi$  electron systems is 1.2 eV.

A last inference which one might draw from the suggestions presented here is that the two benzene rings of dibenzene chromium are perhaps not free to rotate in the way the cyclopentadienyl rings can rotate in ferrocene-like compounds. The five-membered cyclopentadiene ring has no distortion available to it permitting all the ring electron pairs to avoid the metal  $d$  electrons and at the same time to carry the attractive

<sup>18</sup> In this sense, our placement of the perturbed  $a_{1g}$ ,  $a_{2u}$ ,  $a'_{1u}$  and  $a'_{2g}$   $\pi$  orbitals in Fig. 2 is not entirely consistent; we used the exciton model to help justify the assignment of Band IV as a  $\pi \rightarrow \pi^*$  transition, yet placed the perturbed orbital levels as they would be in free benzene, in their unperturbed positions, except for the revised value of  $\beta$ .

<sup>19</sup> R. S. Mulliken, J. Phys. Chem. **56**, 295 (1952).

<sup>20</sup> E. G. Cox, Revs. Modern Phys. **30**, 159 (1958).

ring nuclei with them. The benzenes of dibenzene chromium, on the other hand, can move into a single structure which lowers the  $\pi d$  interaction, and introduces a barrier to rotation. Substitution experiments based on isomer formation might come to mind which would show whether this barrier is larger than, say,  $kT$  at room temperature.

*Note added in proof.* Two articles have appeared recently concerning dibenzene chromium which prompt some comment here. In the first of these [D. A. Levy and L. E. Orgel, *Mol. Phys.* **4**, 93 (1961)], the authors place the  $a_{1g}$  orbitals above the  $e_g$ , on the basis of the magnetic measurements of reference 14. We would like to add to our discussion that this orbital sequence would be acceptable according to the foregoing spectral analysis as follows. As we mentioned in Sec. II, the  $3de_g'$  orbital must be placed below  $4pe_g'$ ; then we must disallow our strong-field approximation enough to keep the  $3de_g \rightarrow 4pe_u'$  transition as part of Band II, using the term-splitting of the configurations as our rationale. Band II still contains  $3da_{1g} \rightarrow 4pe_u'$ , but  $3de_g \rightarrow 4pa_{2u}'$

must lie at very high energy. This assignment has one slightly unattractive feature not previously mentioned. The  $\pi e_u \rightarrow 3de_g'$  transition attributed to Band I has a  $z$  component allowed in both threefold and sixfold symmetry. Rather, its  $x, y$  component disappears in  $D_{6h}$  symmetry. One therefore loses the simple interpretation of the apparent structural and spectral changes associated with the change of state.

The second reference [R. D. Feltham, *J. Inorg. Chem.* **16**, 197 (1961)] contains spectral information similar to that of references 1 and 2, further electron spin measurements and a spectrum of dibenzene chromium itself in cyclohexane solution. No Band I' is reported; a very weak band is found, corresponding to the spin-forbidden transition, a very broad band is formed with  $\lambda_{\max}$  at about 3150 Å, and the absorption rises at short wavelengths, as Band IV appears. Our assignment suggests that Band I would be very weak and possibly undetectable. The breadth of the observed band is not inconsistent with the possibility that it contains both Bands II and III.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 35, NUMBER 1

JULY, 1961

## Quantum Statistical Mechanics of Isotope Effects\*

I. OPPENHEIM

*National Bureau of Standards and Physics Section, Convair, San Diego*

AND

A. S. FRIEDMAN

*National Bureau of Standards and United States Atomic Energy Commission*

(Received December 27, 1960)

Expansions in powers of Planck's constant are utilized in a discussion of isotope effects on the thermodynamic properties of fluid systems. Theoretical calculations of the differences in the equations of state of the hydrogen isotopes and of the helium isotopes are presented and comparison with experimental results are made. Agreement between theory and experiment is excellent.

### 1. INTRODUCTION

SOME considerations for demonstrating the necessity for a quantum statistical treatment of isotope effects are discussed. In statistical mechanics, one obtains expressions for thermodynamic properties of a system in terms of the phase space distribution functions. The distribution functions are derivable, in theory, from a knowledge of intermolecular interactions. For the simple systems being considered in the density

range pertinent for our calculations, the potential energy of the system of  $N$  particles  $U^N$  is considered to be a sum of pair potentials  $U_{ij}$ ,

$$U^N(\mathbf{R}^N) = \sum_{i < j}^N U_{ij}(\mathbf{R}_i, \mathbf{R}_j), \quad (1)$$

where  $\mathbf{R}^N$  is the  $3N$ -dimensional position vector of the  $N$  particles. This discussion will be restricted to spatially uniform fluid systems and it is assumed that the structureless particles are spherically symmetric and that  $U_{ij}$  depends only on the scalar distance  $R$  between particles  $i$  and  $j$ ; i.e.,

$$U_{ij} = U_{ij}(R). \quad (2)$$

\* Supported in part by the U. S. Atomic Energy Commission, Division of Research. A portion of this work is contained in a thesis presented by one of us (I.O.) in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Yale University.