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Preliminary communication

Some additional evidence for the sixfold symmetry of benzene in dibenzenechromium in the vapor phase

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Some time ago an IR-spectroscopic study of gaseous dibenzenechromium involving, one of us[1] produced the first experimental proof of the sixfold symmetry (D_{6h}) of benzene in this complex in the vapor state. This ended a long controversy in the history of which some papers were published which claimed (X ray[2] and IR studies[3-5]) and other papers which denied (X ray[6-8] and IR[9,1]) that benzene in $Cr(C_6H_6)_2$ had a symmetry which was lower (D_{3d}) than that of the free molecule (D_{6h}).

We were interested in additional aspects of the matter and it occurred to us that an elegant possibility was offered by the electron diffraction study[10].

The electron diffraction study had yielded two solutions (the first being the more likely one): benzene as a ligand in $Cr(C_6H_6)_2$ was found to have only one type of carbon–carbon bond (1.423 Å) and hence sixfold symmetry, if the mean C—C vibrational amplitude was the same (0.045 Å) as that of free benzene (0.0454 Å)[11]. On the other hand, two different types of carbon–carbon bonds were possible (hence threefold symmetry), but then the mean C—C vibrational amplitude had to be smaller (0.0435 Å) than that of C_6H_6.

With the IR[1] and the Raman spectra[12] of the complex, the values for the amplitudes above can easily be checked and one solution can be excluded. We have performed such a calculation applying the Σ-matrix procedure described by Cyvin[13]. As the basis of this calculation we used a normal coordinate analysis of benzene as a ligand with D_{6h} symmetry[12], following Wilson's technique[14] with the *G*-matrix given by Crawford and Miller[15].

The results are given in Table 1 (Column A: IR mean C—C vibrational amplitudes for C_6H_6, $Cr(C_6H_6)_2$, $Cr(C_6H_6)_2^+$ and $C_6H_6Cr(CO)_3$; column B: electron diffraction mean C—C vibrational amplitudes for C_6H_6 and $Cr(C_6H_6)_2$). It is clearly seen that the values obtained by the different techniques are very similar. Small deviations of the order of magnitude of 0.001 Å between electron diffraction and vibrational analyses may in general very well be due to the use of non-relativistic electron scattering factors[16]. It also is very clearly seen that all the IR amplitudes are practically identical. If one interprets the trifle differences which are observed as being significant, then the $Cr(C_6H_6)_2$ value is rather larger than that of C_6H_6, while it had to be smaller to allow for a split of the C—C parameter. The value obtained for the cation, $Cr(C_6H_6)_2^+$, is interesting, too, since this molecule was always described to be so different from the neutral complex. In contrast to $Cr(C_6H_6)_2$, $Cr(C_6H_6)_2^+$ was always assigned sixfold symmetry[5,19]. Its mean C—C vibrational amplitude is very much the same as those of the other compounds, which also supports our interpretation. The same is true for $C_6H_6Cr(CO)_3$ which also was claimed[22] to contain threefold benzene but subsequently was found without doubt to have sixfold symmetry in its benzene part[23].

We think that these results provide additional evidence for the sixfold symmetry of benzene in dibenzenechromium in the vapor phase. This statement may be of special interest since publications by other groups have continued the controversy after the IR vapor study[1] was published: one, employing third law entropies being against[17], another[18], employing neutron diffraction, being in favor of a distortion of benzene in $Cr(C_6H_6)_2$. For the vapor phase the situation seems clear, and so the problem has been reduced to the question whether or not the molecule is distorted by crystal forces in the solid state. All this casts some doubts at least on a few qualitative theoretical approximations[20,21] which tried to explain the "distortion" of complexed benzene in dibenzenechromium by invoking metal-ring orbital interactions.

TABLE 1

MEAN C—C VIBRATIONAL AMPLITUDES FOR FREE AND COMPLEXED BENZENE CALCULATED FROM THE VIBRATIONAL SPECTRUM (T = 298°K, set A) AND OBTAINED FROM ELECTRON DIFFRACTION[10,11] (set B)

	set A	set B
C_6H_6	0.0461 Å	0.0454 Å
$Cr(C_6H_6)_2$	0.0462	0.0450
$Cr(C_6H_6)_2^+$	0.0463	–
$C_6H_6Cr(CO)_3$	0.0461	–

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