unknown slopes) or slopes that vary with structure in some systematic way. If this is true it may be more proper to take the H_0 at half-ionization as a real measure of basicity within a series of related compounds than attempt to correct it for solvation by means of a slope which is not known with accuracy.

It will be noted that the H_0 at half-ionization does not change appreciably as the alcohol concentration is varied nor does it change as the slope of the plot is modified. So far in our experience there is no reason to question the published half-ionization points for most Hammett weak bases although as the slopes are better elucidated many thermodynamic pK_a's may be drastically altered. We suggest that some of the difficulties which have been found in kinetic interpretations of reactions involving alcohols are the result of their being very poor Hammett indicators (slopes widely different from unity) so that the fraction ionized does not vary with changing acidity in a way predicted by the H_0 function.

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THE CRYSTAL STRUCTURE AND MOLECULAR STRUCTURE OF DIBENZENECHROMIUM

Sir:

Fischer and Weiss[1] reported the correct unit cell for $Cr(C_6H_6)_2$ which *requires* that the molecule belong to the point group D_{3d} and *permits* it to belong to any group of higher symmetry having D_{3d} as a subgroup. However, they and Ruch[2] proposed a theory of bonding which led them to postulate that the molecule *should* have only a threefold and not a sixfold axis. Evidence from vibrational spectra both for,[3] against[4] and again for[5] threefold symmetry has been reported.

In the meantime, in 1960, Jellinek[6] had reported that using X-ray diffraction intensities for 177 reflections (not further specified) a set of atom positions had been determined, giving for the usual reliability index the impressive value of 6.3%. No details of the data collection or the distribution of data over the reciprocal lattice and very few concerning the refinement were mentioned. The carbon atom positions corresponded to D_{3d} symmetry with planar rings having alternating bond distances of 1.439 and 1.353 Å. with standard deviations of only 0.014 Å.

Ordinarily, a structure would have been considered firmly established under these circumstances, but in this case doubts remained. This was at least partly because a satisfactory molecular orbital treatment of the bonding can be constructed[7] without reduction of the sixfold symmetry of the rings, although distortion of the type invoked by Fischer would not necessarily have any pronounced effect on the bonding and at least one qualitative suggestion of a cause for such distortion has been put forward.[8] A more recent investigation,[9] however, led to the conclusion that there is no

apparent way to account for distortion to D_{3d} symmetry.

Thus, the position is that theoretically, distortion seems unnecessary and not easily explained, while experimentally there has been reported one seemingly reliable evidence for it, although there does not appear to be any other evidence which is decisive either way. It thus appeared that the evidence for low symmetry deserved re-examination and an independent re-investigation of the crystal structure was therefore undertaken. This note is a preliminary report of the results.

Three dimensional data were gathered by usual techniques, but with considerable care, at room temperature, using a Weissenberg camera and $MoK\alpha$ radiation.[10] Levels $hk0$–$hk9$ were recorded on equi-inclination photographs. A total of 270 independent reflections of measurable intensity were recorded and their intensities estimated visually. On upper layers, only the extended spots were used and they were corrected for elongation.[11] Because of the general occurrence of equivalent reflections (hkl, klh, lhk) in the cubic space group, random errors in the photographic records are unlikely to have escaped detection. After Lp corrections, the data were placed on a common scale by intercomparison of films, and approximate absolute scaling and temperature factors were obtained by Wilson's method.[12] Since chromium atoms do not contribute to reflections with mixed indices, separate temperature factors and scale factors for Cr and C atoms were obtained using two Wilson plots. The scale factors were quite close.

A set of trial carbon positions was obtained and a few cycles of least squares refinement were carried out in which the carbon positions, an over-all scale factor and isotropic temperature factors were varied. A residual, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of 0.104 was obtained. The next step, an extremely important one, was concerned with eliminating the effects of spurious discrepancies in scale factors from one set of films to another. In this particular case, the difficulty arises because reflections on the hkl (l even) films can only be placed on the same scale as those from the hkl (l odd) films by comparing different records of spots with mixed indices. These are produced only by the carbon and hydrogen atoms and are thus in general relatively weak. In order to minimize the effect of interfilm scaling errors from this source, the refinement program was modified to permit separate scale factor adjustment for the two classes of data. Three more cycles of full matrix refinement were now carried out, giving the following results (standard deviations in parentheses): C–C 1.386 (0.017) and 1.407 (0.017); Cr–C: 3.132 (0.012), 2.138 (0.012); Cr–center of mean plane of C's: 1.616 (0.010); deviation of each carbon atom from mean plane: 0.004; $R = 0.061$ based on observed reflections, with no unobserved reflection giving $F_c > |F_{min}|$ where $|F_{min}|$ is for the weakest observed reflection; R over all reflections in the range of observation: 0.115.

In view of the fact that the contribution of the hydrogen atoms is not entirely negligible compared to that of the carbon atoms, it was considered important to check their influence upon the above carbon atom positions. A three-dimensional difference Fourier map was there-

(1) E. O. Fischer and E. Weiss, Z. anorg. allgem. Chem., **286**, 142 (1956).

(2) E. Ruch, "Ber. Jahrestagung Chem. Ges. DDR," Leipzig, 1959, p. 125.

(3) H. P. Fritz, and W. Lüttke, "Proc. of the Vth Intern. Conf. on Coörd. Chem. (London), Special Publ. No. 13," The Chemical Society (London), 1959, p. 123.

(4) H. P. Fritz, W. Lüttke, H. Stammreich and R. Forneris, Ber., **12**, 3246 (1959).

(5) H. P. Fritz, "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p. 239.

(6) F. Jellinek, Nature, **187**, 871 (1960).

(7) (a) M. E. Dyatkina and E. M. Shustorovich, Russ. J. Inorg. Chem., **4**, 179 (1959); (b) F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963, p. 174.

(8) R. S. Berry, J. Chem. Phys., **35**, 29 (1961).

(9) D. H. W. den Boer, P. C. den Boer and H. C. Longuet-Higgins, Mol. Phys., **5**, 387 (1962).

(10) An earlier attempt had been made to collect data at liquid nitrogen temperature using an integrating Weissenberg camera but such extremely long exposures were required to record reflections with mixed indices that this procedure was abandoned.

(11) D. C. Phillips, Acta Cryst., **9**, 819 (1956).

(12) A. J. C. Wilson, Nature, **150**, 152 (1942).

fore calculated and scrutinized for indications of the hydrogen atom positions. One set of six (*i.e.*, three in each ring) showed up quite sharply, lying just a little outside the mean plane of the carbon atoms. Hydrogen atoms in the other set showed up rather diffusely. Assigning all hydrogen atoms to positions estimated from the difference Fourier map[13] another cycle of least squares refinement gave for the C–C distances 1.387 (0.017) and 1.387 (0.017).

From the results outlined above, the following conclusions have been drawn:

1. The alternate C–C distances probably differ by less[14] than 0.02 Å. with the mean value being about 1.40 Å.

2. The causes of the difference between the results reported here and those of Jellinek cannot, of course, be identified with certainty at the present. We think it likely, however, that the greater number of reflections used and the inherent superiority of least squares refinement[15] to the difference Fourier method used by Jellinek should make the present results the more reliable ones.

3. While the study described here is not to be considered the final word on the problem,[16] the present results are important in showing, *at the very least*, that the widespread impression that the symmetry of dibenzenechromium has been proved by X-ray methods to diverge greatly from sixfold is not justified. Rather, our results indicate that there is only slight degradation of sixfold symmetry such as can be readily attributed to the crystalline environment and not to any *inherent* tendency of the molecule to have vastly different C–C bond lengths.

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(13) The difference Fourier map also indicated some anisotropy in the motion of the carbon atoms, such that the rings may be assumed to be undergoing torsional motion about the molecular symmetry axis. In consequence of this, the C–C distances represent lower limits and the true ones are probably 0.01–0.02 Å. greater.

(14) The equality, at 1.387 Å., obtained after inclusion of hydrogen atoms is not to be taken literally for various reasons. The important point of the calculation is the demonstration that the inclusion of hydrogen atoms does not *increase*, but instead tends to *decrease*, the difference in alternating C–C bond lengths. The fact that the introduction of the hydrogen atoms also lowers the mean C–C distance is qualitatively reasonable and the magnitude of the effect, ~0.01 Å., seems credible.

(15) The elimination of errors in temperature factors, the opportunity of weighting the data and the possibility of minimizing the effect of interfilm scaling errors are probably of main importance in the present case.

(16) Data collection at low temperature using counter techniques would represent a further refinement.

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THE PREPARATION OF CYCLOPENTADIENYL [*o*-(PHENYLAZO)PHENYL]NICKEL

Sir:

Apart from certain metal azo-dye complexes which can be considered as chelates,[1] the participation of the azo group in delocalized bonding with transition metals comparable to unsaturated carbon systems has not been reported. We wish to report a nickel complex in which the azo grouping, conjugated with unsaturated carbons, is bonded in a manner similar to an alkenyl anion. The complex, structure I, was prepared from dicyclopentadienylnickel and azobenzene both in the absence and presence of a solvent.

In a typical experiment (all manipulations carried out under prepurified nitrogen), 5 g. of dicyclopentadienylnickel and 20 g. of azobenzene were heated at 135° for

(1) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961, Chapter 14.

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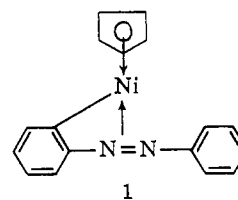
4 hr. After removal of excess azobenzene by sublimation under reduced pressure, the reaction residue was dissolved in low-boiling petroleum ether and chromatographed twice on alumina. During the sublimation of the reaction mixtures, a liquid was collected which was identified as aniline by comparison of its infrared spectrum with that of an authentic sample, and by preparation of acetanilide. The yield of the purple-blue crystalline nickel complex was 2.0 g., m.p. 115–118°. An analytical sample of the complex was prepared by several recrystallizations from petroleum ether followed by an additional chromatographing. The elemental analysis of the purified product, m.p. 118–119°, corresponded to structure I.

Anal. Calcd. for $C_{17}H_{14}N_2Ni$: C, 66.9; H, 4.63; Ni, 19.2; mol. wt., 305. Found: C, 66.7; H, 4.69; Ni, 19.1; mol. wt., 310 (isopiestic). This new complex of nickel is quite stable to oxidation and can be exposed to air without noticeable decomposition. It is soluble in hydrocarbons, ethers, alcohols, carbon tetrachloride and carbon disulfide but insoluble in water. The material is somewhat volatile and can be sublimed in the region of 100° at 10^{-5} mm.

Structure I for the complex is proposed on the basis of both physical and chemical studies. It is diamagnetic,[2] suggesting that nickel has attained kryptonic electron arrangement. The n.m.r. spectrum possesses a group of four resonances relative to tetramethylsilane, at −5.33 (singlet), −6.92 (triplet), −7.93 (quadruplet) and −8.15 (doublet) p.p.m., with respective ratios of 4.8:2.2:6.7:1. The singlet at −5.33 p.p.m., corresponding to five hydrogens, is characteristic of hydrogens on a cyclopentadienyl ring π-bonded to nickel.[3] The remaining resonances have presently not been assigned other than that they are of a complex phenyl hydrogen type.

The presence of an azobenzene type moiety in the complex was demonstrated with the aid of a lithium aluminum hydride reduction. To a cooled suspension of 1.5 g. of lithium aluminum hydride in diethyl ether was added 0.75 g. of the complex in 10 ml. of ether. Work-up of the reaction mixture and chromatography of the residue on alumina with petroleum ether gave, after recrystallization from ethanol–water, 0.061 g. of azobenzene, m.p. 65–67°, with an infrared spectrum identical with an authentic sample. Since it is not apparent how azobenzene itself could be bonded to a cyclopentadienylnickel grouping in the complex and render it diamagnetic, one of the phenyl ring carbons, by the loss of a proton, must also partake in bonding to nickel. This situation was illustrated adequately by reducing the complex with lithium aluminum deuteride which yielded an orange product, m.p. 64–68°, possessing an infrared spectrum similar to azobenzene and containing approximately 10% deuterium. Deuterium was determined with a mass spectrometer on the water formed from combustion of the product. The water of combustion possessed a spectrum for the high mass peaks 17 to 20 and the low masses 2 to 4 quite similar to an artificial mixture of 10% deuterium oxide, 90%

(2) We are indebted to Professor Stanley Kirschner, Wayne State University, for the magnetic susceptibility measurement.

(3) (a) M. Dubeck, *J. Am. Chem. Soc.*, **82**, 6193 (1960); (b) M. Dubeck and A. H. Filbey, *ibid.*, **83**, 1257 (1961).