

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 map¹³ 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 less¹⁴ 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 refinement¹⁵ 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.

Acknowledgment.—This work was generously supported by a grant from the U. S. Army Research Office.

(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.

DEPARTMENT OF CHEMISTRY F. A. COTTON
MASSACHUSETTS INSTITUTE OF TECHNOLOGY W. A. DOLLASE
CAMBRIDGE 39, MASS. J. S. WOOD

RECEIVED MARCH 30, 1963

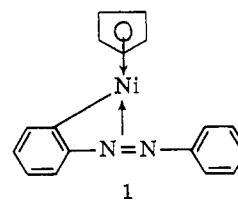
THE PREPARATION OF CYCLOPENTADIENYL [*o*-(PHENYLAZO)PHENYL]NICKEL

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.



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 C₁₇H₁₄N₂Ni: 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).

water by volume. Ultraviolet absorptions support the bonding of the nitrogen system to nickel in the complex as maxima are observed at 252, 268, 345 and 585 $m\mu$ with respective molar extinction coefficients of 14,000, 13,050, 7550 and 6200, in 95% ethanol. This contrasts with the spectrum of azobenzene which has maxima at 230, 318 and 440 $m\mu$ with molar extinctions of 8370, 19,500 and 587. The loss of absorption in the 318- $m\mu$ region, attributed to the conjugation of the unsaturated nitrogen with the phenyl rings, strongly suggests that the nitrogen system in the complex is bonded to nickel in a manner shown in structure I and this bonding allows nickel to attain rare gas structure.

The accumulated experimental evidence is in agreement with the proposed structure of the isolated nickel complex. Although the position of the deuterium label in the liberated azobenzene following deuteride reduction was not determined, it is difficult to visualize, on the basis of steric requirements, bonding between nickel and the phenyl ring at any site other than the *ortho* position. The exact position of nickel relative to the nitrogen system also has not been established, as such refinements can only be determined unequivocally with X-ray diffraction studies.

ETHYL CORPORATION
RESEARCH LABORATORIES
DETROIT, MICHIGAN

JOSEPH P. KLEIMAN
MICHAEL DUBECK

RECEIVED MARCH 27, 1963

2,7-DIACETOXY-*trans*-15,16-DIMETHYL-
15,16-DIHYDROPYRENE. A NOVEL AROMATIC
SYSTEM WITH METHYL GROUPS INTERNAL TO THE
 π -ELECTRON CLOUD¹

Sir:

We wish to report the results of an investigation bearing on two classical problems in the chemistry of aromatic molecules: (1) the question of aromaticity of monocyclic polyenes larger than benzene; and (2) the possibility of having functional groups within the cavity of an aromatic π -electron cloud. The general class of compounds which was chosen for study was that of the *trans*-15,16-dihydropyrenes,^{2,3} and the present communication describes the synthesis of 2,7-diacetoxy-*trans*-15,16-dimethyl-15,16-dihydropyrene (VI), a molecule fulfilling both of the requirements previously mentioned.

The synthesis of VI required seventeen steps and utilized the metacyclophane III as a key intermediate to provide the correct geometry for the final stages. The path taken is presented by listing the intermediate compounds in schematic outline. Each of the steps down to II ($y = -CH_2I$) proceeded in high yield following the general methods outlined previously.² The cyclization of II ($y = -CH_2I$) to give III, m.p. 212.5–213.0, occurred in 55% yield using sodium and tetraphenylethylene and the structure of III is supported by molecular weight data and by the close correspondence of its n.m.r. spectrum to that of 4,12-dimethyl-(2,2)-metacyclophane.^{4,5} Oxidation of III with ferric chloride in chloroform gave directly in 92% yield the bis-dienone IV, m.p. 260° dec., which on treatment with N-bromosuccinimide produced the yellow quinone V, m.p. 265° dec., in 76% yield. That V was a true quinone was indicated by the appearance of a deep blue-green color when it was treated with dithionite. Further, a preparative reduction of V with zinc and acetic

(1) The authors gratefully acknowledge financial support by the National Science Foundation.

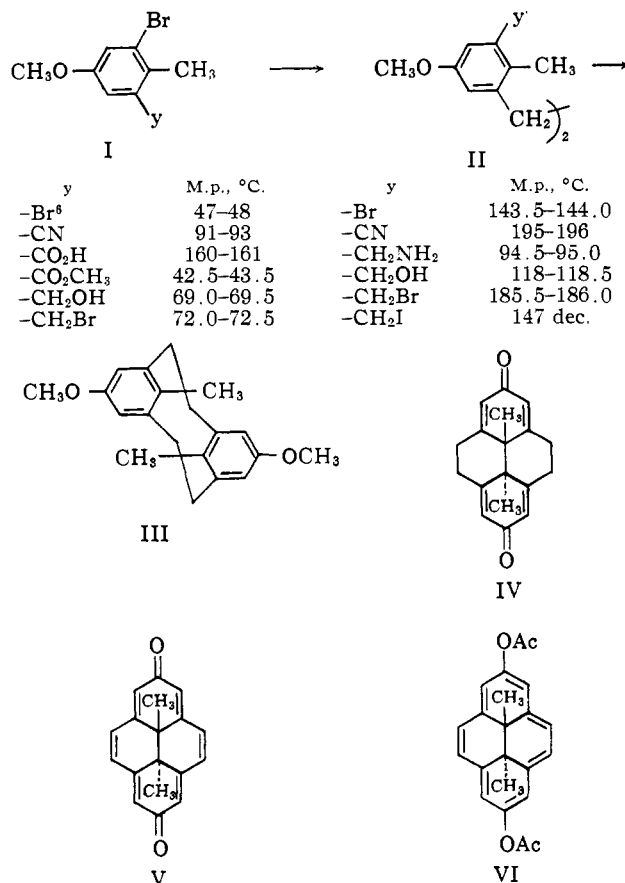
(2) W. S. Lindsay, P. Stokes, L. G. Humber and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

(3) R. W. Griffin, Ph.D. Thesis, University of Rochester, 1960.

(4) D. J. Wilson, V. Boekelheide and R. W. Griffin, *J. Am. Chem. Soc.*, **82**, 6302 (1960).

(5) A. W. Hanson, *Acta Cryst.*, **15**, 956 (1962).

anhydride in the presence of triethylamine effected the separation of brilliant green crystals of the hydroquinone diacetate VI, m.p. 204.5–205.0° softening at 199°, λ_{max} (ϵ) (cyclohexane) 643 (1,840), 466 (10,250), 371 (38,900) and 337 $m\mu$ (97,400), in high yield. As would be expected, hydrolysis of VI and oxidation regenerated the quinone V.



Probably, the most pertinent evidence regarding VI is its n.m.r. spectrum which shows two equal sharp signals at 1.42 and 1.63 τ (8 ring protons), a singlet at 7.50 τ (6 protons of the acetate methyls) and a singlet at 14.03 τ (6 protons of the internal methyls). Thus, the very strong ring current which is clearly evident substantiates the conclusion that VI is aromatic. This result is particularly interesting in view of the elegant work of Sondheimer and his collaborators on the closely related annulenes.^{7,8}

The presence or absence of a ring current has been the basis for describing (18)annulene and 1,8-bisdehydro-(14)annulene as aromatic but (14)annulene as a non-aromatic polyene. The good agreement between the ultraviolet and visible spectra of VI and 1,8-bisdehydro(14)annulene is in keeping with the presence of a 14- π electron aromatic cloud in each and is further indication that the lack of aromaticity in (14)annulene is due to distortion by the internal protons.

Actually, VI is quite stable toward heat, light and air, suggesting that it is also "aromatic" in the classical, non-thermodynamic sense. Again, this is in agreement with the properties of 1,8-bisdehydro(14)annulene but contrasts with (18)annulene in which presumably there is still appreciable repulsion among the internal hydrogens. It should be pointed out that since the

(6) The starting material (I, $y = -Br$) was prepared by methylation of the corresponding phenol (G. Baddeley and J. Plant, *J. Chem. Soc.*, 525 (1943)).

(7) F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey and R. Mason, *J. Am. Chem. Soc.*, **84**, 4595 (1962).

(8) F. Sondheimer, R. Wolovsky and Y. Amiel, *ibid.*, **84**, 274 (1962).