

TABLE I

VARIATION OF DIFFERENTIAL LINE BROADENING WITH CONCENTRATION AT  $-56^\circ$ ; DETERMINATION OF  $k_t$

[I], <i>M</i>	[II], <i>M</i>	$1/r_1 = k_t \text{ sec.}^{-1}{}^a$	$1/r_{11} \text{ sec.}^{-1}{}^a$	$k_t \text{ sec.}^{-1}{}^b$
0.125	0.125	9.1	8.1	8.1
0.167	0.084	9.1	14.7	7.4
0.084	0.167	8.8	3.7	7.4
0.063	0.063	8.8	8.1	8.1
0.083	0.042	8.8	16.1	8.2

<sup>a</sup> From eq. 3. <sup>b</sup> From eq. 7.

Knowledge of the equilibrium constant ( $K_{eq} = k_t/k_r$ ) now makes  $k_r$  accessible. Ultraviolet data,<sup>8</sup> using similar solutions of I as for the n.m.r. experiments, yielded a value of  $K_{eq} = 2.8 \times 10^{-4}$  at  $-56^\circ$ .<sup>9</sup> Using an average value of  $k_t = 8.4 \text{ sec.}^{-1}$ , then  $k_r = 3 \times 10^4 \text{ sec.}^{-1}$ .

The conclusion that exchange between I and II occurs *via* an S<sub>N</sub>1 process agrees with our preliminary observation that factors which affect the exchange rates are those which modify  $k_t$ . Accordingly, rate enhancements are observed with: (a) increasing solvent polarity, (b) increasing halogen polarizability, and (c) cation-stabilizing ring substituents. Work is continuing.

**Acknowledgment.**—The authors thank Professors G. Whiteside, C. G. Swain, and H. Morawetz for helpful discussions.

(8) We thank Dr. R. Waack and Miss M. Doran for the low-temperature ultraviolet data.

(9) This compares to  $K_{eq} = 2.1 \times 10^{-4}$  for I in  $\text{Cl}_2\text{CCHCl}_2$  at  $20^\circ$  [A. G. Evans, A. Price, and J. H. Thomas, *Trans. Faraday Soc.*, **52**, 332 (1956)].

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## The Phenylation of Pyridine-Metal Complexes

Sir:

The chemical reactions of coordinated ligands have been an area of recent interest to others,<sup>1</sup> and also to us in terms of their free-radical chemistry.<sup>2</sup> To further this inquiry, a set of experiments was designed whereby phenyl radicals were caused to react with pyridine dissolved in *N,N*-dimethylformamide and in separate experiments with a group of pyridine-metal complexes dissolved in the same solvent.

A large number of complexes of pyridine were prepared, and the ones indicated in Table I were found to be completely stable to the reaction conditions (all analyses were satisfactory). This stability was ascertained by using the pyridine ligand bands in the infrared.<sup>3</sup> The stable complexes showed no change in the ligand bands when newly dissolved in dimethylformamide, after standing at least 4 days in the dimethylformamide at  $25^\circ$ , and after 4 days in the solvent plus the phenyl source at  $25^\circ$ . However, new

TABLE I

PHENYLATION ISOMER RATIOS

Complex, mole	Phenyl source, mole	2-Phenyl, %	3-Phenyl, %	4-Phenyl, %
Pyridine <sup>a</sup> (0.150)	0.0150	41.1	39.0	19.8
Co(Py) <sub>2</sub> Cl <sub>2</sub> (0.021)	0.0124	66.7	13.1	20.2
Cr(Py) <sub>2</sub> Cl <sub>3</sub> (0.043)	0.0124	45.0	19.0	36.0
Zn(Py) <sub>2</sub> (SCN) <sub>2</sub> (0.049)	0.0124	46.0	23.0	31.8
Mn(Py) <sub>2</sub> (SCN) <sub>2</sub> (0.024)	0.0124	34.9	32.8	32.9
Ni(Py) <sub>2</sub> (SCN) <sub>2</sub> (0.018)	0.0124	23.8	34.5	41.8
Cd(Py) <sub>2</sub> (SCN) <sub>2</sub> (0.049)	0.0124	43.3	33.6	23.2

<sup>a</sup> Uncomplexed.

bands were formed owing to the phenylation of the complexes under the last conditions, but no bands owing to free pyridine. When the decomposition of any complex was evidenced by either a decrease in the intensity of the ligand infrared bands, or a color change, or the formation of a precipitate (silver metal by an oxidation-reduction reaction with the silver complex) over a 5-day period, that complex was discarded. The phenyl source used was *N*-nitroso-*sym*-diphenylurea which was completely decomposed at  $25^\circ$  over a 3-day period under the reaction conditions. This phenyl source was prepared by the known method<sup>4</sup> and also by the reaction of diphenylurea with nitrosylsulfuric acid generated *in situ* by the action of water upon nitrosylsulfuric anhydride.

The pure isomeric phenylpyridines were prepared by the phenylation of pyridine by a standard method<sup>5</sup> and separation of the three phenylpyridines by preparative thin layer chromatography. The picrates of the separated samples agreed with those reported previously.<sup>5</sup> Mixtures of the isomers, both prepared and from the reactions, could be separated and their relative amounts measured by gas chromatography using specially prepared columns. The reliability of the method for isomer determination was checked and the results are: known mixture, 39.1:39.9:21.0; gas chromatographic integration values, 41.5:36.2:22.2; column factor, 0.94:1.10:0.95; and calculated values, 38.6:38.0:23.2. It was shown that the isolation procedures were sufficiently efficient to begin with 0.48 g. of products in a 70.9:18.9:10.1 ratio and obtained 0.47 g. in a 71.0:19.6:9.5 ratio. When these methods were applied to phenylation reaction mixtures involving complexes, the data in Table I were obtained.

A typical reaction involved dissolving 16.7 g. (0.049 mole) of dipyridinezinc(II) thiocyanate in 80 ml. of dimethylformamide, followed by the rapid addition of 3.00 g. (0.124 mole) of *N*-nitroso-*sym*-diphenylurea and allowing the mixture to stand for 3 days. Isolation involved evaporation of the solvent under vacuum, decomposition of the complex with base, filtration, extraction with toluene, acidification, extraction, neutralization, extraction with carbon disulfide, and

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drying. This final solution was used for the gas chromatographic measurement (flame detector) and, as indicated above, accounted for at least 98% of the basic products. The materials identified were: phenylpyridines, 0.217 g., 0.0014 mole; benzene, 0.343 g., 0.0044 mole; diphenylurea, 0.106 g., 0.0025 mole; and aniline, 0.093 g., 0.001 mole. These accounted for 67% of the phenyl radicals. A residue, 0.266 g., was also formed which would account for the rest.

The results show a definite enhancement of substitution in the 4-position of all the complexes but one, and in the 2-position in most cases. It is not evident whether the amount of substitution at the 3-position is decreased or remains the same. The substituent effects can be explained by considering a back donation of electrons to the pyridine ring by the metal ion. This d-p  $\pi$ -electron conjugation would involve a filled  $d_{xz}$  orbital of the metal and its interaction with the  $\pi$ -electron system in the pyridine ring.<sup>6</sup> The back donation to the ligand would be especially effective toward the 2- and 4-positions and is similar to that shown to occur in other coordination compounds.<sup>7</sup>

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### Structure of the Dimer of Tetraphenylcyclobutadiene

Sir:

A three-dimensional X-ray diffraction study of  $C_8$ -Ph<sub>8</sub>,<sup>1,2</sup> where Ph is  $C_6H_5$ , has yielded the octaphenylcyclooctatetraene structure. These results exclude the octaphenylcubane structure,<sup>3</sup> as well as the tetrabiphenylcyclooctane formula<sup>4</sup> which had been rendered improbable earlier on spectroscopic evidence.<sup>5</sup>

We have confirmed the previously reported<sup>3</sup> crystal symmetry of  $I4_1/a$ , the four molecules of  $C_8Ph_8$  per unit cell, and the unit cell dimensions of  $a = 19.49$  and  $c = 10.65$  Å. The compound  $(PhAlNPh)_4$ , in which the Al and N atoms are arranged at the corners of a cube,<sup>6,7</sup> has the same space group and four molecules per unit cell; furthermore, its lattice dimensions of  $a = 20.0$  and  $c = 10.9$  Å. are increased over those for  $C_8Ph_8$  by an amount which seemed consistent with an initial assumption of a slightly smaller cube for the  $C_8$  unit. Consequently, we chose as a trial molecular structure a cube of eight C atoms to each of which was attached a phenyl group having the C-Ph bond along a body diagonal of the cube, and having the  $C_6H_5$  plane oriented

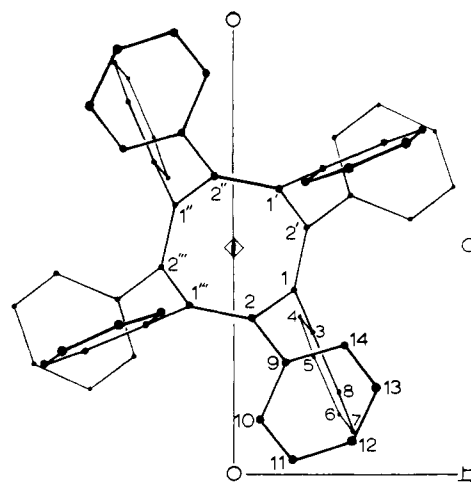


Fig. 1.—The structure and position in the unit cell of one molecule of octaphenylcyclooctatetraene. The origin is at the lower left corner, the  $\bar{4}$  axis is at the molecular center is at  $0^{1/4}1^{1/8}$ , the  $4_1$  axis is at  $x = 1/4, y = 0$ , and the centers of symmetry are shown as circles at  $000, 1/8^1/8^3/8$ , and  $0^{1/2}0$ . Bond distances are  $1-2 = 1.51, 1-2' = 1.35, 2-2' = 2.48, 1-1' = 2.46, 1-3 = 1.50,$  and  $2-9 = 1.50$  Å. The twelve independent C-C distances in the benzene rings have an average distance of  $1.39 \pm 0.01$  Å.

either in the 110 type of plane of the isolated cube or perpendicular to this type of plane. This model, when placed at the four equivalent sites of  $\bar{4}$  symmetry in the crystal, has only the one degree of freedom consisting of arbitrary orientation about the  $\bar{4}$  axis.

A very good approximation to the molecular orientation finally found was obtained by comparison of values of  $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$  computed for various orientations from about 10% of the observed diffraction maxima. The minimum value of  $R$  yielded a structure which later comparison showed was very similar to the  $(PhAlNPh)_4$  structure, kindly communicated to us by W. S. McDonald. However, the C atoms of the previously assumed  $C_8$  cube moved considerably, during the course of least-squares refinement, to the final positions shown in Fig. 1. Clearly, this refinement has yielded the octaphenylcyclooctatetraene structure. The present value of  $R$  is 0.12 for the 1627 observed reflections,  $1.4 \leq F_{hkl} \leq 336$ , and the thermal motion is highly anisotropic. Hence we considered the possibility that octaphenylcubane might be transformed *within the single crystal* to octaphenylcyclooctatetraene upon exposure to X-rays. Therefore, a sample previously unexposed to X-rays was examined first by infrared and then by Raman techniques, exposed to X-rays for a day, and then re-examined by infrared and Raman methods. No evidence of transformation of the molecule by X-ray irradiation could be detected. Hence, we conclude that the original sample as prepared is indeed octaphenylcyclooctatetraene. The intermolecular contacts are, however, primarily determined by the phenyl groups, which are oriented within the molecule in such a way that an  $\alpha$ -H atom of one phenyl group points toward the center of the closest neighboring benzene ring. This suggestion of a "dimple" toward the center of a benzene ring was first noted in the intermolecular packing of the biphenylene crystal.<sup>8</sup>

The internal angles of the tub-shaped cyclooctatetraene (COT) ring are  $120^\circ$ , in agreement with pre-

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