

plex at 0°, perhydrophenanthrene, a mixture of at least four isomers (by v.p.c.), very rapidly rearranged to *trans,syn,trans*-tetradecahydroanthracene. The course of subsequent isomerization was identical with that described above for the rearrangement of *trans,-syn,trans*-tetradecahydroanthracene.

In forthcoming papers, the thermodynamics and probable mechanism of formation of adamantanes from tricyclic saturated hydrocarbons will be discussed; in addition, the detailed infrared, n.m.r., and mass spectrometry of the various intermediate and final products will be presented.

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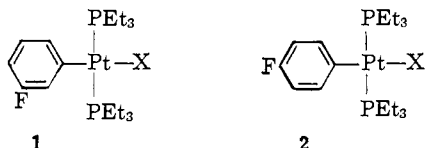
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Electronic Factors in the *trans* Effect

Sir:

I wish to report a technique for discriminating between two electronic factors which contribute to the *trans* effect in the nucleophilic substitution of metal complexes.¹ The F¹⁹ n.m.r. shielding parameters of the *m*- and *p*-fluorophenylplatinum complexes 1 and 2 measure the ability of the fluorophenyl group to compete with the anionic ligand X for the electron density of the central platinum atom. The *meta* parameter varies with the σ -donor character of X as transmitted by the platinum atom while the *para* parameter varies with the π -acceptor nature of X. Since both properties are believed to contribute to the *trans*-activating effect of X, this criterion of electronic character is a useful tool for studies of inorganic reaction mechanisms.



The F¹⁹ n.m.r. shielding parameters of substituted fluorobenzenes are a sensitive probe for electronic effects in aromatic compounds.² Application of this probe to the *m*- and *p*-fluorophenylplatinum complexes 1 and 2 (X = CH₃) shows that there is a strong flow of electron density from the platinum atom to the fluorobenzene ring (see Table I). The positive shielding parameter of 11.7 p.p.m. for 2 puts the bis(phosphine)platinum substituent in a class with strong resonant donors such as hydroxyl and alkoxy. The +4.06-p.p.m. shift for the *meta* compound is much larger than that which would be obtained if the methyl group were attached directly to the ring (+1.15 p.p.m.). The strong shielding effect in both compounds can be ascribed to interaction between the filled platinum d-orbitals and the benzenoid π -orbitals. This interaction enhances the electron density throughout the ring and at the *ortho* and *para* positions in particular.

The shielding parameters of the *m*-fluorophenyl complexes 1 are quite sensitive to changes in the *trans*

(1) The topic of the *trans* effect has been reviewed by F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(2) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

ligand. The shifts presumably represent variations in electron density in the σ -bond system of the complexes

TABLE I
PARAMETERS FOR COMPOUNDS 1 AND 2

Ligand X	F ¹⁹ Shielding parameter ^a (f)		π -Bond criterion ^b (Z)
	1	2	
CH ₃	+4.06	11.70	7.64
C ₆ H ₅	3.5	10.92	7.4
<i>m</i> -FC ₆ H ₄	3.42	10.65	7.23
<i>p</i> -FC ₆ H ₄	3.30	10.79	7.49
CN	2.27	9.32	7.05
Cl	2.13	10.11	7.98
Br	1.97	9.86	7.89
NCS	1.75	9.29	7.54
I	1.56	9.54	7.98

^a The chemical shift in p.p.m. relative to fluorobenzene as an internal standard in an 8-10% solution of the complex in acetone-*d*₆. ^b $Z = f_2 - f_1$.

induced by the σ -donor effect of the *trans* ligand X. The shielding parameter sequence parallels the basicity³ sequence of X as measured in a nonpolar solvent, e.g., CH₃⁻ > C₆H₅⁻ > FC₆H₄⁻, and CN⁻ > Cl⁻ > Br⁻ > I⁻.

The major resonance structure which enhances the electron density in the *para* position of the benzene ring in compound 2 involves overlap of the filled platinum 5d_{xy}-orbital with the adjacent carbon π -orbital. The same d-orbital may also take part in π -bonding with vacant orbitals on the *trans* ligand X. Hence, the F¹⁹ shielding parameter of 2, after correction for inductive effects, provides a criterion of the ability of X to compete with the *p*-fluorophenyl ring for electron density in the d_{xy}-orbital. This criterion, Z (the difference between the parameters of 1 and 2), takes values ranging from 7.05 for the strongly π -bonding cyanide ion to almost 8 for the halide ions which have little or no π -acceptor capacity.⁴ The aryl ligands seem to form substantial π -bonds to the platinum as proposed by Chatt and Shaw.⁵ The fact that halide ions give higher Z values than does methyl, which should be an ideal example of a non- π -bonding ligand, suggests that the halides may actually be weak π -donors.⁴

These experimental results support the postulate that the *trans* effect is, in reality, at least two effects and that either of two types of ligands can produce *trans* activation.¹ Strong donor ligands such as methyl and phenyl weaken the *trans*-metal-ligand bond by polarization of the platinum atom while strong π -acceptor ligands can facilitate nucleophilic substitution in the *trans* position by stabilizing the transition state during the reaction. This combination of effects accounts for the powerful *trans* activation produced by ligands such as cyanide (and probably R₃P) which are both σ -donors and π -acceptors.

The compounds used in this study were prepared by the procedures of Chatt and Shaw.^{3,6} *trans*-Dichlorobis(triethylphosphine)platinum(II) was treated with *p*-fluorophenylmagnesium bromide to give *trans*-di-*p*-fluorophenylbis(triethylphosphine)platinum(II), m.p. 199-200°. A benzene solution of the di-*p*-fluorophenyl

(3) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962), and references cited therein.

(4) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

(6) Satisfactory elemental analyses were obtained for all new compounds.

complex was treated with anhydrous HCl to give *trans*-chloro-*p*-fluorophenylbis(triethylphosphine)platinum(II), m.p. 103–104°. The other halogen and pseudo-halogen complexes (2: X = Br, I, SCN, and CN) were prepared by simple metathetical reactions of the chloro compound. The aryl and methyl compounds (2: X = C₆H₅, *m*-FC₆H₄, and CH₃) were obtained by reaction of the appropriate Grignard reagents with the chloride. The *m*-fluorophenylplatinum compounds were prepared by similar procedures. The *trans* configurations of all the compounds studied were confirmed by the proton magnetic resonance technique of Jenkins and Shaw.⁷ The CH₃ resonance of the triethylphosphine ligands appeared as a characteristic five-line structure ($J = 7.8 \pm 0.3$ c.p.s.) owing to coupling with the CH₂ protons and with the two *trans* P³¹ nuclei equivalently.

(7) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

CONTRIBUTION NO. 1021

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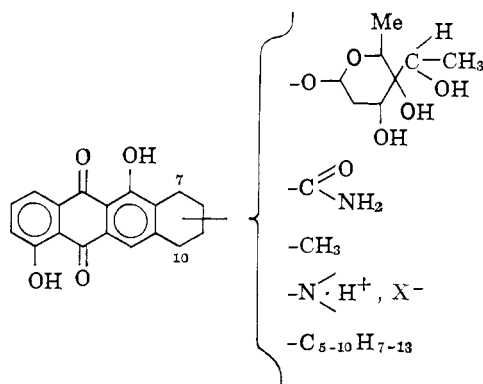
WILMINGTON, DELAWARE

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The Structure of Isoquinocycline A. An X-Ray Crystallographic Determination¹

Sir:

Recently, a partial structure has been proposed for isoquinocycline A based on spectroscopic, degradative, and chemical studies.² Two major and several minor features of the antibiotic have been established or suggested. These results are summarized as follows



This communication presents the complete structure of the molecule and its relative stereochemistry as determined by the X-ray method.³

A satisfactory partial structure for the antibiotic was obtained through the use of the weighted isomorphous replacement method.⁴ In this way, it was demonstrated that structures can be solved in the *noncentrosymmetrical* case employing isomorphous replacement procedures with the information that is available from only *two* isomorphous derivatives (the

(1) This research has been supported by the National Institutes of Health, U. S. Public Health Service, and Lederle Laboratories Division, American Cyanamid Co.

(2) D. B. Cosulich, J. H. Mowat, R. W. Broschard, J. B. Patrick, and W. E. Meyer, *Tetrahedron Letters*, No. 7, 453 (1963); *ibid.*, No. 13, 750 (1964).

(3) A preliminary account of this work was presented at the Annual American Crystallographic Association Meeting held in March, 1963, at the Massachusetts Institute of Technology, Cambridge, Mass.

(4) G. Kartha, *Acta Cryst.*, 14, 680 (1961).

hydrochloride and the hydrobromide in the present example).⁵ The partial structure (22 atoms plus bromine) was then augmented, in steps, using more conventional techniques until 58 atoms (excluding hydrogen) were finally fixed.

The two salts, crystallized from dioxane–water, were found to be orthorhombic, with space group P2₁2₁2₁, and their cell dimensions agreed within 0.2–0.3%. The density of the hydrobromide gave an X-ray molecular weight of 886 which, from elemental analysis, placed the asymmetric unit at C₄₀₋₄₁H₄₇₋₅₃N₂O₁₃₋₁₄Br. Considering the empirical formula favored for the antibiotic,² the high carbon and oxygen content suggested that dioxane and possibly water of solvation were present in the crystals.

The positions of the chloride and bromide ions were determined from three principal difference Patterson projections employing coefficients of the type $(|F|_{\text{Br}} - |F|_{\text{Cl}})^2$, where $|F|_{\text{Br}}$ and $|F|_{\text{Cl}}$ are the structure amplitudes of the hydrobromide and hydrochloride salts, respectively. Their *x*-coordinate proved to be special ($x \sim 0$) and, consequently, generated an unwanted mirror plane of symmetry at $x = 1/2$ in the weighted electron density. The relative and absolute scales of the two isomorphs, requisite to the weighted isomorphous replacement method, were first obtained by Wilson's method and then verified and improved upon from two-dimensional structure factor and electron density considerations. The zero contribution of the replaceable electrons to certain classes of two-dimensional reflections and a comparison of peak heights (excluding bromide and chloride) in projected electron densities served to obtain a self-consistent relative scale which was then fixed on an absolute basis by comparing the observed projected peak heights and peak shapes of the ions with those based on computation, systematically varying an isotropic thermal parameter for the ions. The weights for the observed structure amplitudes, functions of $|F|_{\text{Br}}$, $|F|_{\text{Cl}}$, and the replaceable electron contribution, were computed but they proved to be, in general, inapplicable in a direct manner. A very large number of them had an absolute value greater than unity and these usually ranged between ± 10 . Such behavior was assumed to be the result of observational errors in intensity so their effect on the weight computation was assessed by approximating the standard error of the weight in terms of the estimated standard error of the structure amplitudes. Then, somewhat arbitrary but rather stringent criteria were employed to select acceptable weights. These were used to compute a weighted electron density. The density contained 146 peaks greater than $1 \text{ e}\text{\AA}^{-3}$ in the asymmetric unit, of which about 73 were related by mirror symmetry. A 22-atom partial structure (the tetracyclic nucleus and its hydroxyl and carbonyl substituents) was easily derived and it served as a starting point for the use of more conventional methods to obtain the remainder of the structure.

The structure of isoquinocycline A is shown above, from which most of the stereochemistry is self-evident. The antibiotic consists of five fused rings joined to a pyrrolopyrrole *via* a spiro atom and also to a sugar-like

(5) The author wishes to thank the Organic Chemical Research Section, Lederle Laboratories Division, American Cyanamid Co., for supplying these samples.