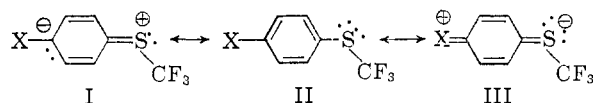


TABLE II  
 $\sigma$ -PARAMETERS

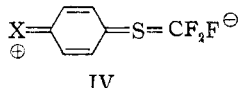
	From ionization of $\text{XC}_6\text{H}_4\text{CO}_2\text{H}^b$							
	$\text{XC}_6\text{H}_4\text{CO}_2\text{H}$		$\text{XC}_6\text{H}_4\text{NH}_2^+$		Cl	OCH <sub>3</sub>	SCH <sub>3</sub>	$\text{O}=\text{CCH}_3$
	OCF <sub>3</sub>	SCF <sub>3</sub>	OCF <sub>3</sub>	SCF <sub>3</sub>				
$\sigma_m$	+0.39	+0.40	+0.47	+0.46	+0.37	+0.11	+0.14	+0.37
$\sigma_p$	+0.35	+0.51	+0.28	+0.64	+0.23	-0.27	-0.01	+0.42
$\sigma_I^a$	+0.51	+0.31	+0.50	+0.40	+0.47	+0.21	+0.22	+0.32
$\sigma_R^a$	-0.13	+0.17	-0.23	+0.22	-0.25	-0.47	-0.24	+0.10

<sup>a</sup> Calculated using equations 1, 6 and 3 with appropriate  $\alpha$  and  $\rho_1$  values from Table II, Reference 12. <sup>b</sup> Values are from H. H. Jaffee, *Chem. Rev.*, **53**, 222 (1953); F. G. Bordwell and P. J. Barton, *J. Am. Chem. Soc.*, **78**, 854 (1956); F. G. Bordwell and G. C. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952).

eters and presented arguments for expansion of the valence shell of the sulfur in the  $\text{SCOCH}_3$  and  $\text{SCN}$  groups.<sup>15</sup> The  $\sigma_R$  parameters for the  $\text{SCF}_3$  group are considerably larger positive values and provide much more striking evidence for large contributions of form III.



The contribution of resonance form I must be minor, but becomes significant in the transition state for substitution of the ring by an electrophilic reagent since the orientation<sup>8</sup> is ortho-para and not meta. For a  $\text{SCH}_3$  group, resonance form I must make the major contribution rather than form III. Contribution from resonance form IV, involving fluoride ion "no-bond" structures, is considered unlikely on



the basis of comparison with resonance effects for the  $\text{CF}_3$  and  $\text{SF}_3$  groups.<sup>16</sup>

Observations in support of the above discussion also have been made for the  $\text{OCF}_2\text{CF}_3$ ,  $\text{OCF}_2\text{CF}_2\text{H}$  and  $\text{SCF}_2\text{CF}_2\text{H}$  groups and will be presented in detail in a future publication.

(15) The expansion of the sulfur outer shell was recently reviewed by G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(16) W. A. Sheppard, publication in preparation.

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NUCLEOTIDE AND OLIGONUCLEOTIDE  
COMPOSITIONS OF THE ALANINE-, VALINE-, AND  
TYROSINE-ACCEPTOR "SOLUBLE" RIBONUCLEIC  
ACIDS OF YEAST

Sir:

The alanine-, valine-, and tyrosine-acceptor "soluble" ribonucleic acids (RNAs) of yeast recently have been purified by countercurrent distribution.<sup>1</sup> Table I gives the results of analyses of the nucleotide compositions of the three purified RNAs. The alanine RNA, in comparison with the other two, has a very low content of adenylic acid (Ap) and a high content of guanylic acid (Gp), and possibly contains less pseudouridylic

(1) J. Apgar, R. W. Holley and S. H. Merrill, *J. Biol. Chem.*, in press. (For a recent review of the role of "soluble" RNA in protein synthesis see P. Berg, *Ann. Rev. Biochem.*, **30**, 293 (1961)).

acid (PsUp). The valine and tyrosine RNAs differ little in nucleotide composition.<sup>2</sup>

The analyses in Table I are consistent with the formulas for the purified RNAs.<sup>3</sup>

Alanine RNA:  $\text{pGp}[(\text{Ap})_{10}(\text{Cp})_{26}(\text{Gp})_{28}(\text{Up})_{17}(\text{P}_s\text{Up})_3]\text{A}$

Valine RNA:  $\text{pGp}[(\text{Ap})_{16}(\text{Cp})_{22}(\text{Gp})_{24}(\text{Up})_{16}(\text{P}_s\text{Up})_4]\text{A}$

Tyrosine RNA:  $\text{pGp}[(\text{Ap})_{18}(\text{Cp})_{22}(\text{Gp})_{25}(\text{Up})_{14}(\text{P}_s\text{Up})_4]\text{A}$

As indicated in Table I, the partition coefficients of the valine and tyrosine RNAs in the

TABLE I

NUCLEOTIDE COMPOSITIONS OF PURIFIED ALANINE-, VALINE- AND TYROSINE-ACCEPTOR RIBONUCLEIC ACIDS OF YEAST<sup>a</sup>

Nucleotide	RNA, Mole %		
	Alanine	Valine	Tyrosine
Ap <sup>b</sup>	12.1	19.1	21.7
Cp	29.9	27.5	26.7
Gp	33.7	29.5	30.2
Up	20.8	19.0	17.1
PsUp	3.7	4.9	4.4
Partition coefficient <sup>c</sup>	0.12	0.21	4.2

<sup>a</sup> Alkaline hydrolysates of 1 mg. of the RNAs were chromatographed on Dowex 1 columns 0.2 × 15 cm. according to the procedure of W. E. Cohn and E. Volkin, *Nature*, **167**, 483 (1951). The values given are averages of three or more determinations, and are not corrected for the terminal nucleoside and nucleoside diphosphates. <sup>b</sup> The abbreviations used are: Ap, adenylic acid; Cp, cytidylic acid; Gp, guanylic acid; Up, uridylic acid; and PsUp, pseudouridylic acid. <sup>c</sup> Partition coefficients of the purified RNAs in a countercurrent distribution solvent system composed of phosphate buffer, formamide and 2-propanol (see ref. 1).

countercurrent distribution solvent system differ by a factor of 20 although these two RNAs differ little in nucleotide composition. Presumably the different partition coefficients are a result of differences in nucleotide sequence. To obtain information on nucleotide sequences, pancreatic ribonuclease digests of the three purified RNAs were chromatographed on DEAE-Sephadex.<sup>4</sup> The results of the analyses are shown in Fig. 1. In the chromatographic patterns, the mononucleotides, cytidylic acid (peak at fraction 37) and uridylic acid (peak at fraction 50), are followed by dinucleotides and higher oligonucleotides. The peak at

(2) Previous analyses of fractions across the countercurrent distribution pattern indicated little change in nucleotide composition except at the end of the pattern, where the alanine RNA is found.

(3) The formulas assume terminal guanosine diphosphate (M. F. Singer and G. L. Cantoni, *Biochim. et Biophys. Acta*, **39**, 182 (1960)) and terminal adenosine (H. G. Zachau, G. Acs and F. Lipmann, *Proc. Natl. Acad. Sci.*, **44**, 885 (1958)) although these have not yet been established for the purified RNAs.

(4) The procedure used was a modification of that of M. Staehelin, E. A. Peterson and H. A. Sober, *Arch. Biochem. Biophys.*, **85**, 289 (1959). The use of DEAE-Sephadex (Pharmacia Fine Chemicals, Rochester, Minn.) in place of DEAE-cellulose is strongly recommended.

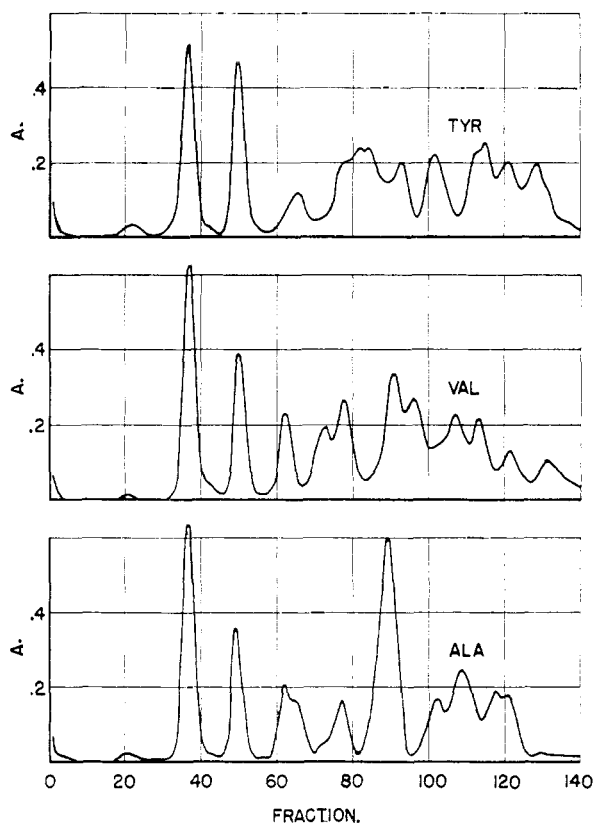


Fig. 1.—Absorbancies (A) at 260  $m\mu$  of fractions obtained by chromatography of pancreatic ribonuclease digests of 1.5 mg. each of the purified alanine-acceptor RNA (bottom curve), valine-acceptor RNA (middle curve), and tyrosine-acceptor RNA (top curve) on DEAE-Sephadex. (The column,  $0.25 \times 50$  cm., was eluted with an increasing gradient of ammonium carbonate produced by using 120 ml. of water, 120 ml. of water, and 116 ml. of 0.75 *M* ammonium carbonate respectively, in three chambers of a Varigrad (see ref. 4). The volume of the fractions was 2.2 ml.)

fraction 90, very pronounced in the digest of the alanine RNA, is believed to be GpUp, the last of the dinucleotides to be eluted.

Comparison of the three curves in Fig. 1 indicates that there is hardly a single oligonucleotide that occurs to the same extent in any two of the RNAs. The chromatographic analyses on DEAE-Sephadex are highly reproducible and even the smaller differences in the curves are believed to be real.

It is clear that the alanine-, valine-, and tyrosine-acceptor "soluble" RNAs of yeast differ greatly in structure. The differences between these three RNAs are much more complex than would be required by simple hypotheses of information transfer by nucleic acids.

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### MOLECULAR STRUCTURE OF $C_8H_8Fe(CO)_3$

Sir:

There have been a number of suggestions<sup>1,2,3,4,5,6</sup> that the cyclooctatetraene (COT) ring in  $C_8H_8Fe(CO)_3$  is planar, and one suggestion<sup>7</sup> that the tub form, like that established for free cyclooctatetraene<sup>8,9,10</sup> and its silver complex,<sup>11,12</sup> occurs in this compound. A similarly large number and greater variety of suggestions for the geometry of the  $C_8H_8$  ring in  $(OC)_2FeC_8H_8Fe(CO)_3$  were shown to be incorrect, when the unsuspected chair form was proved.<sup>13</sup> We show here that yet another geometry, a dihedral form not included in any of the above predictions, occurs for the cyclooctatetraene ring in  $C_8H_8Fe(CO)_3$ .

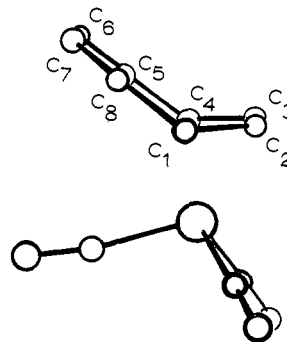


Fig. 1.—The structure of  $C_8H_8Fe(CO)_3$ : bond distances are  $C_1-C_2 = C_3-C_4 = 1.42$ ,  $C_2-C_3 = 1.42$ ,  $C_1-C_5 = C_1-C_8 = 1.45$ ,  $C_6-C_6 = C_7-C_8 = 1.34$ ,  $C_6-C_7 = 1.49$ ,  $Fe-C_1 = Fe-C_4 = 2.18$ ,  $Fe-C_2 = Fe-C_3 = 2.05$ ,  $Fe-C$  (carbonyl) = 1.80 (av.),  $C-O = 1.13$  (av.) all  $\pm$  about 0.02 Å. Bond angles are  $C_1-C_2-C_3 = C_2-C_3-C_4 = 124.6^\circ$ ,  $C_3-C_4-C_5 = C_2-C_1-C_5 = 132.4^\circ$ ,  $C_4-C_5-C_6 = C_1-C_5-C_7 = 133.2^\circ$ ,  $C_5-C_6-C_7 = C_3-C_7-C_6 = 131.8^\circ$ , all  $\pm$  about  $1^\circ$ , and to be compared with  $135^\circ$  in the regular plane octagon. The angle between normals to the two planes in  $C_8H_8$  is  $41^\circ$  in  $C_8H_8Fe(CO)_3$ .

A total of 856 observed X-ray diffraction maxima from a single crystal of symmetry Pnam with four molecules in a unit cell of dimensions  $a = 6.54$ ,  $b = 13.46$  and  $c = 11.51$  Å. has yielded an agreement factor of  $R = \frac{\sum |Fo| - |Fc|}{\sum |Fo|} = 0.091$ . The molecular structure (Fig. 1) shows that the  $Fe(CO)_3$  group is attached to a "buta-

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- (2) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 336 (1960).
- (3) D. A. Brown, *J. Inorg. and Nuclear Chem.*, **10**, 39 (1959); **10**, 49 (1959).
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- (5) P. L. Pauson, *Proc. Chem. Soc. (London)*, 297 (1960).
- (6) L. E. Orgel, "An Introduction to Transition Metal Chemistry: Ligand Field Theory," John Wiley and Sons, New York, N. Y., 1960, p. 159.
- (7) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1960).
- (8) H. S. Kaufman, H. Mark and I. Fankuchen, *Nature*, **161**, 165 (1948).
- (9) J. Bregman, private communication.
- (10) O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).
- (11) F. S. Mathews and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 4745 (1958).
- (12) F. S. Mathews and W. N. Lipscomb, *J. Phys. Chem.*, **63**, 845 (1959).
- (13) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 489 (1961).