by adsorption of an oriented monolayer of a polar-non-polar compound. Many pure liquids which normally spread on clean surfaces of metals were found at 20° to exhibit large contact angles on the monolayer-covered surface. Thus systematic measurements of the surface tension (γ_{LV°) and the equilibrium contact angle (θ_E) have permitted the determination of the spreading coefficient ($S_{b/a}$), work of adhesion (W_A), and free energy decrease on immersion (f_{SL}). Reports have been presented of similar studies on several low-energy surfaces including polytetrafluoroethylene (a surface covered primarily by $-CF_2-$ groups),[2] polyethylene (primarily a $-CH_2-$ surface),[3] and monolayers of *n*-octadecylamine adsorbed on platinum (a surface covered with $-CH_3$ groups).[4] In the studies cited, liquids with unusually low surface tensions such as perfluorotributylamine ($\gamma_{LV^\circ} = 16.3$ dynes/cm.) spread as a duplex film.

In the present work θ_E was measured for more than ninety diverse pure liquids having surface tensions ranging from over 73 to as low as 13.4 dynes/cm. on surfaces of polished platinum, copper and glass which had been modified by adsorption of a close-packed, oriented monolayer of *n*-perfluorodecanoic acid.

Examples of the remarkably large contact angles encountered are: hexadecane (72°), octane (56°), benzene (58°), ethylene glycol (81°), perfluorotributylamine (26°), hexachlorobutadiene (77°), polymethylsiloxane heptadecamer (62°), carbon disulfide (59°), water (102°), and mercury (152°). No liquid was found for which $\theta_E = 0°$. Comparison of other results[2,3,4] for these same liquids shows that the solid coated with an oriented monolayer of perfluorodecanoic acid is the most non-wettable surface ever reported. The contact angles (θ_{CF_3}) for most liquids in contact with this surface and the contact angles on polytetrafluoroethylene (θ_{CF_2}), on an adsorbed film of octadecylamine (θ_{CH_3}) and on polyethylene (θ_{CH_2}) all decrease in the relative order $\theta_{CF_3} > \theta_{CF_2} > \theta_{CH_3} > \theta_{CH_2}$. From the values of f_{SL} it is possible to estimate that γ_{S°, the free surface energy of such a film of perfluorodecanoic acid, does not exceed 25 ergs/sq. cm. The much lower surface energy is basically the reason for the recent observations[5] of a much lower coefficient of dry friction for a solid tetrafluoroethylene polymer as compared with polyethylene.

Many exceptions were found to the generalization in the literature[6] that non-polar compounds spread on non-polar solids. For example, the contact angles of carbon tetrachloride, cyclohexane and *m*-xylene on the monolayer of perfluorodecanoic acid were found to be 60, 62 and 71°, respectively.

This investigation shows that the $-CF_3$ group can be expected to occupy an interesting and unique place in surface chemistry. Compounds such as perfluorodecanoic acid are examples of a new class of amphipathic or surface-active organic compounds with $-CF_3$ groups and one or more adsorbable polar groups at opposite portions of the molecule. Such compounds possess both highly hydrophobic and organophobic properties and when close packing of $-CF_3$ groups can occur, they will have even more unusual resistance to chemical attack by bulk liquids. They may also act when adsorbed on smooth solids as excellent boundary lubricants provided the carbon skeleton of the molecule has a configuration permitting the formation of a sufficiently condensed film.

A report of the entire investigation will be made in the near future.

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RECEIVED JANUARY 28, 1952

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PREPARATION AND PROPERTIES OF A HIGHLY ACTIVE ADRENOCORTICOTROPIC HORMONE PREPARATION[1]

Sir:

By a combination of two published methods[2,3], we have obtained a highly active adrenocorticotropic (ACTH) preparation from sheep pituitary glands. The physicochemical properties of this preparation are highly at variance with previous reports[4,5]; this warrants the present communication.

The acid–acetone extract of fresh sheep glands was fractionated with NaCl as described previously[2]; 10 g. of the NaCl precipitate was dissolved in 0.1 *M* acetic acid and adjusted to *p*H 3.5–4.0. This was followed by the oxycellulose adsorption technique of Astwood, *et al.*[3] From 1 kg. of sheep pituitaries, approximately 200 mg. of highly potent ACTH was obtained. When assayed by the adrenal ascorbic acid depletion test,[6] this product, designated as Preparation E, had a potency of 30–50 USP units per milligram. This indicates a virtually complete recovery of the hormone.

Analysis of a sample of Preparation E gave the following data: N, 16.1%, S, 0.7%, cystine, nil, tryptophan, 3%, and tyrosine, 5%. The preparation was not dialysable through cellulose casings (Visking), and had a sedimentation constant, S_{20}, of 0.8 *S*. As shown in Table I, partial pepsin and acid hydrolysis caused no loss of ascorbic acid depleting activity.

Electrophoresis on Munktell 20 filter paper was carried out in borate buffers of various *p*H and of ionic strength 0.1, at 4°, according to the technique of Kunkel and Tiselius,[7] using crystalline lysozyme as a point of reference for the migration rate of Preparation E. The paper was divided into origin,

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TABLE I

PARTIAL PEPSIN AND ACID HYDROLYSIS OF PREPARATION E

Experiment	Dose, μg.	No. of rats	Average ascorbic acid depletion, mg./100 g. adrenals	Estimated ACTH potency, USP units/mg.
Starting material	0.05	22	84	30
Pepsin[a]	0.05	15	96	52
Acid[b]	0.03	16	132	(270)

[a] 100 mg. Preparation E and 1.25 mg. crystalline pepsin were dissolved in 50 cc. 0.01 *M* HCl and kept at 37° for 3 hr. [b] 1% solution of Preparation E in 0.2 *M* HCl was kept at 100° for 3 hr.

anode and cathode sections according to the ninhydrin-reactive areas. These sections were cut out and eluted with 0.1 *M* HCl for nitrogen determination and bioassay. Results are summarized in Table II; it is evident that part of the ACTH activity migrated to the cathode at *p*H 8 and stayed in the origins at *p*H 9 and 10, while at *p*H 12 it was the anodic fraction which possessed most of the hormonal potency. Thus, it may be concluded that the isoelectric point of the component with which the ACTH activity is associated is below that of the crystalline lysozyme and is located in the neighborhood of *p*H 9, indicating the basic nature of the hormone.

TABLE II

NITROGEN DISTRIBUTION AND BIOLOGIC ACTIVITY OF FRACTIONS OBTAINED FROM PAPER ELECTROPHORESIS OF ACTH PREPARATIONS AT VARIOUS *p*H

*p*H	Fractions from paper electrophoresis	Nitrogen distribution, %	ACTH potency, USP units/mg.
12	Origin	16	5
	Anode	84	7
10	Origin	84	40
	Anode	9	0
	Cathode	7	0
9	Origin	75	50
	Anode	11	0
	Cathode	14	0
8	Origin	36	30
	Anode	10	0
	Cathode	54	70

Further purification of Preparation E by various techniques is being investigated, and results will be reported in subsequent communications. The accompanying letter discusses the further purification of Preparation E by cellulose column chromatography.

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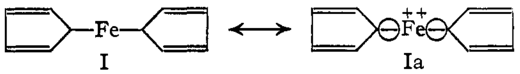
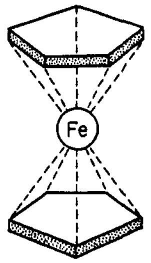
THE STRUCTURE OF IRON *BIS*-CYCLOPENTADIENYL

Sir:

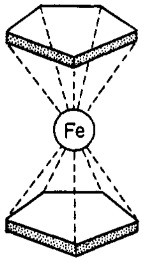
In a recent publication, Kealy and Pauson[1] described the preparation of a compound, $C_{10}H_{10}Fe$, which was formulated as dicyclopentadienyl iron (I ⟷ I*a*). This substance was found to be very stable toward acids and bases, and its isolation stands in striking contrast to the failure of previous investigators to prepare stable organo-iron compounds. These circumstances led us to consider whether an alternative to the structure (I ⟷ Ia) might be more nearly in accord with the unique character of Kealy and Pauson's compound. The equal unsaturation of each of the carbon atoms of the cyclopentadienyl anion suggested that two such units might form covalent bonds to ferrous iron symmetrically. The evidence summarized below provides strong support for the resulting structure (II).



I ⟷ Ia



II



III

Iron biscyclopentadienyl is diamagnetic, with $\chi_{\mathrm{mole}}^{25^\circ} = -125 \times 10^{-6}$ cgsu. The infrared absorption spectrum contains in the 3–4μ region a single sharp band at 3.25μ, which indicates the presence in the compound of C–H bonds of only one type. The ultraviolet spectrum shows maxima at 326 mμ ($\epsilon = 50$) and 440 mμ ($\epsilon = 87$), and rising end absorption of moderate intensity ($\epsilon = 5250$ at 225 mμ). The dipole moment is effectively zero (0.05 *D*). The compound has detectable vapor pressure at 0° and resists pyrolysis at 470°.

Iron biscyclopentadienyl is readily oxidized to a blue cation $[Fe(C_5H_5)_2]^+$. The blue color observed by Kealy and Pauson to accompany dissolution of the iron compound in sulfuric or nitric acid is undoubtedly attributable to this change. Oxidation may be effected anodically, by air in the presence of acids, or by halogens, ferric chloride or ceric sulfate. Especially convenient are aqueous silver sulfate or *p*-benzoquinone in organic solvents in the presence of acids. The cation is reduced by stannous chloride. Polarographic studies indicate an oxidation–reduction potential of −0.59 v. The cation has been isolated as the crystalline tetrachlorogallate (*Anal.* Calcd. for $C_{10}H_{10}FeGaCl_4$: C, 30.25; H, 2.54; Fe, 14.02; Ga, 17.52; Cl, 35.70. Found: C, 30.47; H, 2.77; Fe, 13.97; Ga, 17.52; Cl, 35.76.) and the picrate (*Anal.* Calcd. for $C_{16}H_{12}N_3O_7Fe$: C, 46.35; H, 2.92; N, 10.13; Fe, 13.48. Found: C, 45.99; H, 3.27; N, 10.05; Fe, 13.43.). Most salts with common anions are readily soluble in water; however, a pale blue silicotungstate precipitates from acid solutions. The perchlorate in 1 *N* perchloric acid showed $\lambda\lambda_{\max.}$ 253 mμ ($\epsilon = 13{,}300$) and 619 mμ ($\epsilon = 360$). For the picrate, $\chi_{\mathrm{mol}}^{25^\circ} = +2140 \times 10^{-6}$ cgsu.; the effective paramagnetic moment ($\mu_{\mathrm{eff}} = 2.26$ B.M.) suggests the presence of one unpaired electron, as in the ferricyanide ion ($\mu_{\mathrm{eff}} =$ 2.33 B.M.).

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[1] Kealy and Pauson, *Nature*, **168**, 1039 (1951).