Anal. Calcd. for $C_{14}H_{12}Cl_2$: C, 66.94; H, 4.82. Found: C, 67.08; H, 4.89.

Acknowledgment. The author is indebted to Mr. Fred Baiocchi who verified many of the original observations by repetition of the experiments, and also performed the lithium syntheses.

Kansas City 10, Mo.

[Contribution from the Aeronautical Research Laboratory, Wright Air Development Division,
Air Research and Development Command]

Urea Complexes of Partially Fluorinated Esters[1]

JACK RADELL and JOSEPH W. CONNOLLY

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The effect of fluorine on the ability of a partially fluorinated unbranched ester to form a urea channel complex was found to be predominantly steric and not polar. Complex formation depended upon the number of unfluorinated chain atoms referred to as anchor length and upon the location of the anchor in either the alkyl or acyl moieties of the ester. Knowing the anchor length of the shortest homologue forming a complex, the conformational analysis of an immobilized ester trapped in the prism of urea was determined. The x-ray powder diffraction data were used to determine the presence of urea complexes by indicating the presence of tetragonal urea, hexagonal complex, or a mixture of both. The most stable complexes showed no interplanar spacings for tetragonal urea. The less stable complexes partially dissociated giving characteristic spacings for urea and complex.

Because 2,2-difluorooctane forms a urea complex, the presence of two fluorine atoms upon a single carbon atom in a linear chain does not prevent complex formation.[2] Whether two or more fluorinated carbon atoms linked together in the chain would likewise permit complexing is not known.

EXPERIMENTAL

All complexes were prepared[3] by adding 30 drops of the sample[4] to 4.5 ml. of urea-methanol solution (0.15 g. urea/ml. of methanol) in a test tube. The tube was stoppered and shaken for 30 seconds and allowed to stand at 4° for 24 hr. The crystals that formed were filtered with suction and washed with 10 ml. of absolute ethanol at 4°. The product was vacuum-dried at 4° (1 mm.) over anhydrous calcium chloride for 24 hr. No crystals formed when the urea-methanol solution was used as a blank. In some cases tetragonal urea crystallized from the urea-methanol solution after a noncomplex forming compound had been added.

The dried urea complexes were finely ground with a mortar and pestle and applied to the surface of a roughened glass slide. The interplanar spacings and relative intensities were obtained using the Norelco X-ray diffractometer with a Geiger tube detector at 35,000 volts and 15 milliamps with a scanning rate of 1° per min. A General Electric recorder was used to obtain the data.

The following normal fluorinated acids and alcohols failed to form a complex: CF_3COOH, C_2F_5COOH, C_3F_7COOH, $C_5F_{11}COOH$, $C_7F_{15}COOH$, $C_9F_{19}COOH$, CF_3CH_2OH, $C_3F_7CH_2OH$, $H(CF_2)_2CH_2OH$, $H(CF_2)_4CH_2OH$, $H(CF_2)_6CH_2OH$, $H(CF_2)_8CH_2OH$ and $H(CF_2)_{10}CH_2OH$. From this and the knowledge of which partially fluorinated esters will form complexes, one may conclude that esters of perfluoro acids with either α,α-dihydroperfluoro alcohols or α,α,ω-trihydroperfluoro alcohols will not form a complex; no members of either aforementioned class of hydroperfluoro alcohols, or perfluoro acid formed a complex.

From Table II it can be determined which compounds formed a pure complex, which caused the crystallization of pure urea, and which complexes partially dissociated giving the characteristic patterns of both. The compounds present in Table I and missing from Table II produced no crystalline material under complexing conditions.

In each series of esters where two homologues caused urea only to crystallize, the anchor lengths for the two esters were one and two less, respectively, than the minimum anchor length required for complex formation in that series. The shorter of the two caused the deposition of less urea. In all cases complexes of the higher homologues showed no evidence for dissociated urea which has a characteristic interplanar spacing line in the interval 4.00 to 4.04 Å. This line is most useful because it is relatively strong and does not occur in the x-ray powder diffraction patterns of any of the complexes. The most characteristic line for the urea complexes occurs between 4.11 and 4.17 Å. Other interplanar spacings useful for characterizing a urea complex appear at 3.55–3.64 Å and 7.13–7.19 Å. These spacings show a greater variation in intensity than does the 4.11–4.17 Å spacing. In a homologous series forming urea complexes the relative intensity of the 3.55–3.64 Å and 7.13–7.19 Å shows, in general, a gradual increase as the anchor length of the complexed molecule increases. This same trend[3] is observed for the urea complexes of alkylsilanes.

All measured cross-sectional diameters are maximum values of the planar zigzag conformation obtained from Stuart-Briegleb molecular models. This maximum is less than the maximum obtained from any other configuration.

DISCUSSION

The cross-sectional diameter of the fluorinated monoesters (Series II–VI, Table I) is 5.6 Å compared to 4.8 Å for the corresponding unfluorinated esters, because the effective radius of fluorine (1.3 Å) is 1.3 times greater than hydrogen (1.0 Å). The correspondingly bulkier fluorinated ester would be expected to form a less stable urea com-

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(1) Presented before the International Symposium on Fluorine Chemistry in Birmingham, England, July 14–17, 1959.

(2) W. J. Zimmershied, R. A. Dinerstein, A. W. Weitkamp, and R. F. Marschner, *Ind. Eng. Chem.*, **42**, 1300 (1950).

(3) J. Radell and P. D. Hunt, *J. Am. Chem. Soc.*, **80**, 2683 (1958).

(4) The preparation of these compounds will be described in a separate publication.

TABLE I

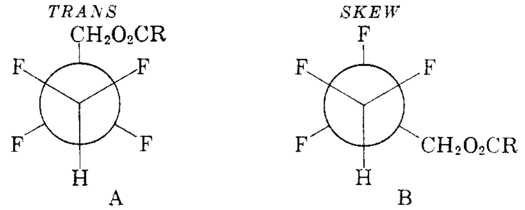
SUMMARY OF UREA FORMING ABILITY OF PARTIALLY FLUORINATED ESTERS

Series	Unbranched Esters	n Noncomplex Formers	n Complex Former	Anchor Length[a] of Shortest Complex Former	Cross-Sectional Diameter A[b]	Number of Fluorine Atoms
I	$CH_3(CH_2)_nCO_2CH_2CF_3$	2	3-6	7	5.1	3
II	$CH_3(CH_2)_nCO_2CH_2(CF_2)_2H$	2, 3	4	8	5.6	4
III	$CH_3(CH_2)_nCO_2CH_2(CF_2)_3F$	2, 3	4-6	8	5.6	7
IV	$CH_3(CH_2)_nCO_2CH_2(CF_2)_4H$	2, 3	4-6	8	5.6	8
V	$C_3F_7CO_2(CH_2)_nCH_3$	4, 5	6, 7, 9	9	5.6	7
VI	$C_5H_{11}CO_2(CH_2)_nCH_3$	5, 6	7, 8	10	5.6	11
VII	$CF_3CO_2(CH_2)_nO_2CCF_3$	5				
VIII	$C_3F_7CO_2(CH_2)_nO_2CC_3F_7$	4-6				
IX	$C_3F_7CH_2O_2C(CH_2)_nCO_2CH_2C_3F_7$	4, 5	7, 8			
X	$C_3F_7CH_2O_2C(CF_2)_3CO_2(CH_2)_nO_2C(CF_2)_3CO_2CH_2C_3F_7$	3, 5				

[a] Number of chain atoms not bearing fluorine. [b] Maximum cross-sectional diameter of the planar zigzag conformation measured on Stuart-Briegleb models.

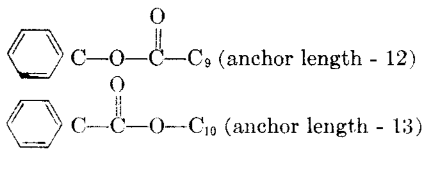
plex based upon the behavior of other bulky molecules.[3,5] In addition to the steric effect, information was sought as to whether the electronegativity of fluorine would have any effect on the complexing ability of partially fluorinated esters. To determine the relative influence of the steric and inductive effects of fluorine in the formation of urea complexes, the shortest homologues of series I–IV in Table I which formed a complex were examined. Each of these esters with fluorine exclusively in the alkyl part showed that an increase in the number of fluorine atoms from 3 (series I, $n = 3$) to 4 (series II, $n = 4$) is associated with an increase of 7 to 8 of the anchor length. When the number of fluorine atoms was increased from 4 to 7 (series III, $n = 4$) and 7 to 8 (series IV, $n = 4$) the anchor length remained unchanged. A comparison of the cross-sectional diameters of the shortest complex formers in Series I–IV, Table I, shows that anchor length varies as does the cross-sectional diameter of the molecule. Series II–IV had the same cross-section and the same anchor length for the respective shortest homologues complexing. In series I the anchor length and the cross-sectional diameter of the shortest complexing homologue was less. The importance of the steric effect of fluorine is far greater than the inductive effect of fluorine as the variation in the complexing ability of the smallest homologue of each series bears a direct relationship to the maximum cross-sectional diameter of the planar zigzag conformation of the ester and not to the number of fluorine atoms present in the alkyl part.

Two conformers of the series II ester in Table I are shown in the planar zigzag form using the Newman projection formula.



Form A had a measured cross-sectional diameter of 5.6 Å; form B had a measured cross-sectional diameter of 5.2 Å. The actual immobilized conformer present in the urea complex was determined in the following way. All esters with fluorine in the alkyl part of the molecule and with a measured cross-sectional diameter of 5.6 Å (Series III and IV, Table I) had an experimentally determined minimum anchor length of 8 for urea complex formation. Where fluorine was in the alkyl part of the molecule and the measured cross-sectional diameter was 5.1 Å (Series I, Table I), the minimum anchor length for urea complex formation was 7. Of the two possible Series II planar zigzag conformers, A was chosen as the conformation in the complex because the shortest homologue forming a urea complex had a minimum anchor length of 8. Conformer A would be preferred for polar and steric reasons as well.

The effect of fluorine varies depending on whether it appears in the alkyl or acyl portion of the ester. A minimum anchor length of 8 is required for urea complex formation in Series III (Table I). In contrast, the minimum anchor length required for complex formation in Series V (Table I) is 9, although the maximum cross-sectional diameter of both esters is 5.6 Å. A similar difference is noted when a bulky group appears in an unfluorinated ester on the acyl or alkyl side. The following two esters with a bulky phenyl group are the shortest homologues of each which form a urea complex:[5]


$$C_6H_5{-}C{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_9 \text{ (anchor length - 12)}$$
$$C_6H_5{-}C{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_{10} \text{ (anchor length - 13)}$$

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(5) E. V. Truter, *J. Chem. Soc.*, 2416 (1951).

TABLE II

INTENSITIES[a] OF INTERPLANAR SPACINGS OF UREA INCLUSION COMPOUNDS, Å

n-R	Anchor Length[b]	7.13–7.19[c]	4.37–4.44	4.11–4.17	4.00–4.04	3.80–3.90	3.55–3.64	3.40–3.41	3.28–3.29	Urea Inclusion Compounds
MONOESTERS $RCOOCH_2CF_3$										
C_3H_7	6				1.00		0.05			−
C_4H_9	7	0.30	0.20	1.00	0.70	0.15	0.75	0.40		+
C_5H_{11}	8	0.50		1.00	0.40		0.80	0.10	0.15	+
C_6H_{13}	9	0.10		1.00			0.20	0.05	0.05	+
C_7H_{15}	10	0.35	0.10	1.00		0.15	0.85	0.30	0.15	+
$RCOOCH_2CF_2CF_2H$										
C_3H_7	6				1.00		0.05			−
C_4H_9	7				1.00		0.05			−
C_5H_{11}	8	0.20	0.05	1.00	0.40	0.05	0.60	0.15	0.10	+
$RCOOCH_2CF_2CF_2CF_3$										
C_3H_7	6				1.00		0.05			−
C_4H_9	7				1.00		0.05			−
C_5H_{11}	8	0.35		1.00	0.70		0.40	0.30	0.20	+
C_6H_{13}	9	0.20	0.10	1.00	0.10		0.30	0.10	0.10	+
C_7H_{15}	10	0.25	0.05	0.40			1.00	0.10	0.05	+
$RCOOCH_2CF_2CF_2CF_2CF_2H$										
C_3H_7	6				1.00					−
C_4H_9	7				1.00					−
C_5H_{11}	8	0.10		0.45	1.00	0.10	0.20	0.10	0.05	+
C_6H_{13}	9	0.10	0.10	1.00	0.20	0.30	0.40	0.30	0.20	+
C_7H_{15}	10	0.30		1.00			0.60	0.25	0.10	+
$CF_3CF_2CF_2COOR$										
C_7H_{15}	9	0.05		1.00	0.30		0.40	0.10		+
C_8H_{17}	10	0.20	0.10	0.90	1.00	0.20	0.80	0.25	0.15	+
$C_{10}H_{21}$	12	0.80		0.95			1.00	0.25		+
$CF_3CF_2CF_2CF_2CF_2COOR$										
C_6H_{13}	8				1.00		0.05			−
C_7H_{15}	9				1.00		0.05			−
C_8H_{17}	10	0.40		1.00	0.05		0.60	0.10		+
C_9H_{19}	11	0.30	0.05	1.00	0.05		0.60	0.45	0.05	+
DIESTERS										
$C_3F_7CH_2O_2C(CH_2)_7CO_2CH_2C_3F_7$	13	0.15	0.15	0.40 (4.21 Å)	1.00	0.20	0.30 (3.69)	0.25	0.25	+
$C_3F_7CH_2O_2C(CH_2)_8CO_2CH_2C_3F_7$	14	0.10	0.10	1.00 (4.21 Å)	0.60	0.10	0.40	0.30	0.15	+
$C_3H_7CO_2(CH_2)_5O_2CC_3H_7$	15	0.20		1.00		0.25	0.50	0.60	0.30	+

TABLE II (*Continued*)

n-R	Anchor Length[b]	7.13-7.19[c]	4.37-4.44	4.11-4.17	4.00-4.04	3.80-3.90	3.55-3.64	3.40-3.41	3.28-3.29	Urea Inclusion Compounds
				MONOESTERS[d] (NONFLUORO)						
$C_3H_7CO_2C_2H_5$	7	0.64 (7.05Å)		1.00 (4.08Å)	0.69 (3.97Å)	0.14 (3.77Å)	0.18 (3.64Å) 0.90 (3.52Å)	0.13 0.45 (3.37Å)		+
$C_4H_9CO_2C_2H_5$	8	0.85 (7.06Å)	0.07 (4.33Å)	1.00 (4.10Å)	0.15 (3.97Å)	0.23	0.85	0.23 (3.37Å)		+
$C_5H_{11}CO_2C_2H_5$	9	0.75 (7.08Å)	0.05 (4.33Å)	0.86 (4.09Å)	0.05 (3.97Å)	0.07 (3.93Å) 0.22	1.00 (3.54Å)	0.38 (3.37Å)	0.08 (3.25Å)	+
$C_6H_{13}CO_2C_2H_5$	10	0.68 (7.08Å)	0.12 (4.33Å)	0.95 (4.09Å)		0.32	1.00	0.48 (3.37Å)	0.16 (3.25Å)	+
$C_7H_{15}CO_2C_2H_5$	11	0.58 (7.02Å)	0.07 (4.34Å)	1.00 (4.09Å)		0.22	0.87 (3.54Å)	0.42 (3.36Å)	0.06 (3.25Å)	+
$C_8H_{17}CO_2C_2H_5$	12	0.50 (7.08Å)	0.07 (4.34Å)	1.00 (4.10Å)		0.19	0.87	0.67 (3.38Å)	0.07 (3.26Å)	+

[a] Relative intensity; 1.0 the strongest. [b] See *a* Table I. [c] CuKα radiation. [d] Commercially obtained.

In the case of the diesters the information is more obscure. The anchor length of the smallest molecule forming a complex is greater for diesters than for monoesters. This is shown in Table I for Series VIII and IX. The picture is further complicated by the fact that the anchor length varies depending on whether the unfluorinated part of the molecule is a dihydric alcohol or a dibasic acid.

The shortest unfluorinated diester reported to form a complex is diethyl malonate[6] with an anchor length of 9. On the other hand, the shortest unfluorinated amyl monoester forming a complex is the acetate[5] with an anchor length of 8. These results parallel our observations (Table I) made on the partially fluorinated mono- and diesters.

The data indicate that the relative effectiveness of the methylene groups in their contribution toward the minimum anchor length requirements of esters to form urea complexes depends upon whether the methylene group occurs in the alkyl or acyl part of the monoesters. In order to determine this relative contribution free of steric effects a series of ethyl esters of unfluorinated *n*-aliphatic alcohols was compared with the amyl esters for urea complex forming ability. Ethyl butyrate with an anchor length of 7 was the shortest of the ethyl esters which formed a complex. Amyl acetate[5] with an anchor length of 8 was the shortest amyl ester forming a complex. Although both had the same cross section, we observed that methylene groups more effectively enhance urea complex formation when they occur in the acyl rather than the alkyl moiety of the molecule. This same generalization may also be applied to esters containing a bulky constituent. In Table I the cross-sectional diameter of Series III and IV are the same, but larger than the cross-sectional diameter of the corresponding unfluorinated esters. When the fluorine occurred in the alkyl part of the molecule, the minimum anchor length in the acyl part necessary for complex formation was 8. Here all but one of the methylene groups occurred in the acyl part. When the fluorine occurred in the acyl part and the methylene groups in the alkyl moiety of the ester (Series V and VI, Table I), an anchor length of at least 9 was necessary for complex formation. In no case has a molecule with a maximum cross-sectional diameter in the planar zigzag conformation of over 6 Å been reported to form a urea complex. As the maximum cross-sectional diameter of the molecule in the planar zigzag conformation increases over that of an unbranched hydrocarbon (4.6 Å), a compensatory increase in anchor length is required to permit complex formation. This was also demonstrated by the work on urea complexes of alkylsilanes.[3]

Although the steric effect of fluorine predominates, this does not mean that the polar effect is

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(6) R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 80, 2683 (1958).

unimportant. For example, although series V and series VI (Table I) both have the same cross-sectional diameters in the planar zigzag conformation, the minimum anchor length is 10 for the latter and 9 for the former. This may be due to a change in the I effect resulting from an increase in the number of fluorine atoms in the molecule from 7 to 11.

Several methods have been previously employed to determine the relative stabilities of the urea inclusion compounds of a homologous series: the dissociation constant at a fixed temperature,[7] the measured heats of formation[2,8] for the inclusion compound, and the use of the dissociation temperatures of the inclusion compounds.[9] A fourth method which was used in our laboratory involves the use of x-ray powder diffraction data. In this and earlier[3] research it was noted (Table II) that the shortest and next to the shortest homologue which showed the characteristic interplanar spacings for complexes also showed spacings for dissociated tetragonal urea. Urea spacings were relatively stronger for the complex of the shorter homologue. Complexes of still higher homologues than these two give characteristic spacings for complex only.

Fluorinated esters containing a sufficiently long unbranched unfluorinated segment can form a urea complex. This generalization can be safely extended to molecules other than esters, *e.g.*, alcohols, acids, amines, etc., so long as the functional group does not increase the maximum cross-sectional diameter of the planar zigzag conformation beyond 6 Å.

The properties of the urea complexes of the fluorinated esters are similar to those of the unfluorinated complexes. The former have transition points[9] and x-ray powder diffraction patterns characteristic of the urea complexes of unfluorinated compounds. Both are made and decomposed in the same manner. No fluorinated ester with an anchor length of less than 7 (see Table I) formed a complex.

The applications which may be made of this technique are essentially the same as for the urea complexes of unfluorinated molecules. These applications (separation, purification, characterization, and storage) have been listed in detail elsewhere.[10]

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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(7) O. Redlich, O. M. Gable, L. R. Beason, and R. W. Miller, *J. Chem. Soc.*, 4153 (1950); E. V. Truter, *Chem. Process Eng.*, **35,** 75 (1954).

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[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION][1]

Preparation and Some Reactions of the Vinyl Ester of Maleopimaric Acid

J. B. LEWIS, W. D. LLOYD, AND G. W. HEDRICK

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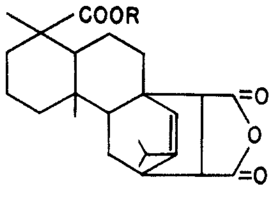
Maleopimaric acid has been vinylated. The vinyl ester has been characterized, its reactions with alcohols and cyclohexylamine have been delineated and it has been copolymerized with vinyl acetate and vinyl chloride.

Levopimaric acid, a constituent of gum oleoresin, condenses at room temperature with maleic anhydride to form the Diels-Alder addition compound[2] maleopimaric acid, 6,14-dihydrolevopimaric acid-6,14-*endo*-α,β-succinic anhydride (I). Most of the resin acids in conventional rosin react with maleic anhydride under vigorous conditions to form I.[3] There are no recorded preparations of the vinyl ester of this acid.

I R = H
II R = Vinyl
III R = Ethyl



Vinyl esters of the resin acids in rosin have been reported by Reppe.[4] Robinson[5] has prepared the vinyl esters of disproportioned and catalytically reduced rosin. Schildknecht,[6] however, states

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(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) (a) R. G. R. Bacon and L. Ruzicka, *Chem. & Ind. (London)*, 546 (1936). (b) H. Wienhaus and W. Sandermann, *Ber.*, **69,** 2202 (1936).

(3) V. M. Loeblich, D. E. Baldwin, and R. V. Lawrence, *J. Am. Chem. Soc.*, **77,** 2823 (1955).

(4) Walter Reppe (to I. G. Farbenindustrie, AKF.), U. S. Patent **2,066,075,** Dec. 29, 1936.

(5) J. C. Robinson, Jr. (to Hercules Powder Co.), U. S. Patent **2,615,012,** Oct. 21, 1952.

(6) C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley & Son, Inc., New York, N. Y., 1952, Chap. 5, p. 385