tion spectra to the remarkably short limit of 1565 Å. using *n*-perfluoroöctane as a solvent.[3]

The fluoro spectrum is peculiarly free of any visible vibrational structure. The 3100 cm.$^{-1}$ blue shift of the $N \rightarrow V$ transition on complete fluorination is to be compared with a blue shift of 500 cm.$^{-1}$ in para-fluorotoluene with respect to toluene itself. This seems to indicate a shift of about 500 cm.$^{-1}$ per F. Spectra being determined on di- and tri-fluoro derivatives will indicate whether this result holds for the intermediate cases. These blue shifts are probably related to the high ionization potential of atomic fluorine, higher than that of any other combining element, and may represent increased ionization potential of the ring system with increased fluorine substitution.

Further detailed analyses of these and other fluorine-substituted benzenes are under way. It is hoped that a tetrafluoro- and a hexafluorobenzene will soon become available.

(3) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **16**, Nov. (1948).

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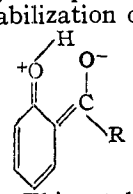
RECEIVED SEPTEMBER 1, 1948

MOLAR REFRACTION AND HYDROGEN BONDING

Sir:

The exaltations, 0.6 and 0.8 ml., observed in the molar refractions (D line) of salicylaldehyde and *o*-hydroxyacetophenone have been attributed[1] to the stabilization of the highly polar resonance structure  by intramolecular hydrogen bonding. This stabilization increases the mobility of the π electrons and thereby increases the polarizability of the molecules.

It occurred to the authors that similar exaltations should be observed in hydrogen bonding solvents for compounds having electron releasing and electron attracting groups at the ends of conjugated chains. The highly polar structure $R_2N^+{=}C_6H_4{=}CHO^-$ contributing to *p*-dimethylaminobenzaldehyde, for example, should be stabilized preferentially by solvent molecules having positive hydrogen atoms. These exaltations have been observed. The molar refraction obtained for this compound in benzene, 51.4 ml., is increased by 1.7 ml. in chloroform and 2.9 ml. in alcohol. Somewhat smaller exaltations have been observed in chloroform and alcohol for anisaldehyde and *p*-nitroanisole.

It was anticipated that the highly polar structure $H_2N^+{=}C_6H_4{=}C(CH_3){-}O^-$ contributing to *p*-aminoacetophenone would be stabilized in alcohol to a greater extent than in dioxane, as the former solvent can form hydrogen bonds with both the amino hydrogens and the carbonyl oxygen. The molar refraction of this compound was observed to increase from 44.3 in dioxane to 45.87 in ethyl alcohol. A similar increase was observed for *p*-nitroaniline.

The molar refraction of diethyl ketone in benzene, 25.12, increases only to 25.22 and 25.21 in chloroform and ethyl alcohol, indicating that hydrogen bonding does not result in any significant increase in polarizability for molecules that are not stabilized by the contribution of highly polar resonance structures.

This research is being continued to study the relative effects of various terminal groups, of double and triple bonds in the conjugated chain, and of mixed solvents on this exaltation.

(1) Curran, THIS JOURNAL, **67**, 1835 (1945).

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RECEIVED SEPTEMBER 15, 1948

THE ISOLATION OF A SUBSTANCE WITH Rh HAPTEN ACTIVITY

Sir:

It has been reported by Carter[1] that ether extraction of Rh-positive red blood cells produced a crude extract containing Rh hapten. We have been able to isolate from such extracts of pooled (A, B, AB and O) Rh-positive human cells a crystalline compound, m. p. 156.9–157.2°, having activity in dilutions of 1:5000 as measured by complement-fixation with anti-Rh_0 serum.[1c,2]

Crude extract[3] prepared according to Mrs. Carter's directions[1a] was freed of phospholipids (*ca.* 25–50% of the material) by precipitation from ether with acetone and the soluble portion was chromatographed from pentane saturated with 95% methanol on silica gel impregnated with the same solvent. A number of fractions containing crude cholesterol were obtained followed by fractions which yielded glistening needles by recrystallization from ether–pentane or chloroform–pentane solution, m. p. 156.9–157.2°. From 979 mg. of crude extract, 80 mg. of the pure hapten was obtained.

(1) (a) Carter, *Am. J. Clinical Path.*, **17**, 646 (1947); (b) Carter, *Am. J. Obst. and Gynecology*, **55**, 1051 (1948); (c) Carter, *J. Immunology*, in press.

(2) We are very grateful to Mrs. Bettina Carter, of the Institute of Pathology, Western Pennsylvania Hospital, Pittsburgh, Pa., for carrying out the assay of Rh activity by complement fixation according to Kolmer (Kolmer and Boerner, "Approved Laboratory Techniques," 4th ed., D. Appleton–Century, New York, N. Y., 1945, p. 674).

(3) We are indebted to Dr. E. D. Campbell and H. J. Henry of Eli Lilly and Company for several samples of crude extract and to Dr. C. S. Culbertson, South Bend Medical Foundation, and Dr. S. O. Levinson, Michael Reese Research Foundation, Chicago, for samples of blood cells.

Anal. Calcd. for $C_{12}H_{18}O_6$: C, 59.49; H, 7.49. Found: C, 58.97, 59.80; H, 7.73, 7.84.

The acid was optically inactive and gave no methoxyl by Zeisel determination. It was soluble in alkali but precipitated on addition of carbon dioxide; neutral equivalent, 246–268. Titration of a purer sample with a Beckmann *p*H meter indicated a pK_a of 10 ± 0.5 and a neutral equivalent of 230 ± 5. It gave no color with ferric chloride, sublimed unchanged and was recovered unchanged after boiling for one hour with alcoholic alkali, after refluxing with pyridine–acetic anhydride and after treatment with semicarbazide acetate for two days. The ultraviolet absorption at 2220 Å. had log ϵ = 2.38, decreasing steadily with increasing wave length. In alkaline solution the curve was shifted 350 Å. toward the visible, with a maximum between 2350–2450 Å.; log ϵ = 2.74. Work designed to elaborate the structure of this compound is in progress.

The crude cholesterol fractions contained a different neutral hapten, not yet isolated in pure form, but active in dilutions of 1:100,000. Perhaps these two substances are reponsible for two of the Rh subgroups.

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RECEIVED AUGUST 16, 1948

(4) Eli Lilly and Company Fellows 1946–1948.

THE CONFIGURATION OF ISOMERIC 1,2- AND 1,3-DICHLOROPROPENES

Sir:

Some question has recently arisen concerning the configuration of the isomeric 1,2- and 1,3-dichloropropenes. Huntress and Sanchez-Nieva[1] report the preparation of the lower-boiling isomer of the 1,2-compound (76° isomer) and state that the configuration of the two stereoisomers is still undetermined. (The other isomer boils at 93°.) In the case of the 1,3-dichloropropenes, the alpha or low-boiling isomer was assigned the trans configuration by Hatch and Roberts[2] due to the fact that, in the presence of cuprous chloride, it was more slowly hydrolyzed than was the beta or high-boiling isomer. Andrews and Kepner[3] questioned this choice, and indicated that no definite assignment could be made on the basis of available experimental evidence.

We wish to report results dealing with the dipole moments of these materials. The pertinent data is given in Table I.

The dipole moments of the 1,2-compounds seem to indicate beyond any possible doubt that the 76° isomer is the *trans* form. The small dipole moment which it does have apparently arises from resonating structures involving the methyl group.[4]

TABLE I

DIPOLE MOMENT DATA FOR SOME ISOMERIC DICHLOROPROPENES AT 30°

Isomer	P_∞ (cc.)[a]		μ (Debye units)	
1,2-Dichloropropene (76° isomer)	43.4		0.84	
1,2-Dichloropropene (93° isomer)	123.0		2.20	
1,3-Dichloropropene (alpha or 104° isomer)	99.5	1.92	1.78[b]	1.77[c]
1,3-Dichloropropene (beta or 112° isomer)	86.0	1.73	1.81[b]	1.66[c]

[a] Determined by the method of Rogers and Roberts, *ibid.*, **68**, 844 (1946). Benzene was used as solvent. [b] From vapor phase data by Oriani and Smyth, *J. Chem. Phys.*, **16**, 930 (1948). [c] From the "Data Sheet" on 1,3-dichloropropenes published by Shell Chemical Corporation, dated 8/4/47.

The dipole moments for the 1,3-dichloropropenes, as listed in the table, are somewhat conflicting. It would appear that the moment of the *cis* compound could not be less than that of the *trans* form. Thus our data as well as that of the Shell Company support the assignment of the *cis* configuration to the alpha or low-boiling isomer, while the data of Smyth gives so little difference in the isomers that little choice is possible.

(4) *Cf.* Rogers, THIS JOURNAL, **69**, 1243 (1947).

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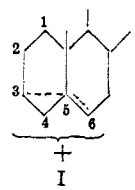
RECEIVED SEPTEMBER 9, 1948

EXCHANGE AT THE 6-POSITION OF *i*-CHOLESTERYL METHYL ETHER

Sir:

We have recently[1] suggested that the predominant mechanism which operates for the conversion of cholesteryl *p*-toluenesulfonate to the *i*-ether involves ionization to an intermediate ion I which has the cationic charge distributed between positions 3 and 6 and which reacts more rapidly with methanol at position 6 than 3.



I

Postulating the same ion I as an intermediate in the well-known[2] rearrangement of an *i*-compound to a normal one, one would expect, in the acid-catalyzed conversion of *i*-methyl to *n*-ethyl ether, prior formation, to a large extent, of the *i*-ethyl ether. This we have now been able to confirm.

(1) Huntress and Sanchez-Nieva, THIS JOURNAL, **70**, 2813 (1948).
(2) Hatch and Roberts, *ibid.*, **68**, 1196 (1946).
(3) Andrews and Kepner, *ibid.*, **69**, 2230 (1947).

(1) Winstein and Adams, THIS JOURNAL, **70**, 838 (1948).
(2) McKennis, *ibid.*, **69**, 2565 (1947).