function for (11b). By substituting (13) in (11b) and taking the sum of the values for all the electrons, one obtains σ_z of the molecule

$$\sigma_z = (e^2/2mc^2)\sum_i [(\langle x_i^2 + y_i^2)/r_i^3\rangle - \langle x_i\rangle\langle x_i/r_i^3\rangle - \langle y_i\rangle\langle y_i/r_i^3\rangle] \quad [14b)$$

Averaging the molecular values for all orientation of a molecule gives

$$\sigma_{av} = (\sigma_x + \sigma_y + \sigma_z)/3 = (e^2/3mc^2)\sum_i [\langle 1/r_i\rangle - \langle x_i\rangle\langle x_i/r_i^3\rangle - \langle y_i\rangle\langle y_i/r_i^3\rangle - \langle z_i\rangle\langle z_i/r_i^3\rangle] \quad (15b)$$

Equations 14b and 15b are identical with those proposed by Ito.[3] If one assumes that $h = xy$, eq. 11b gives the formula proposed by Das and Bersohn.[7]

The comments on the form of h which were given under the discussion of diamagnetic susceptibility hold also for the nuclear magnetic shielding constant.[16] Therefore eq. 14b and 15b should give satisfactory results for (a) the types of molecules to which (14a) and (15a) are applicable, and (b) for the effects of electrons localized at atoms relatively distant from the nucleus under study; (14b) and (15b) have been applied in a few cases.[3]

III. Electronic Polarizability

The effective Hamiltonian of an electron under an external electric field E may be expressed in the form of (1) with

$$\chi^{(1)} = ezE, \quad \chi^{(2)} = 0 \quad (2')$$

where the field is along the z-axis. By the use of the variational function (4), the energy W of the perturbed electron may be expressed in the form of (7) with

(16) H. F. Hameka, *Mol. Phys.*, **1**, 203 (1958).

$$A = W_0 + eE\langle z\rangle$$
$$B = 2eE(\langle zg\rangle - \langle z\rangle\langle g\rangle) \quad (9')$$
$$C = (\hbar^2/2m)(\langle(\nabla g)^2 + (\nabla h)^2\rangle)$$

The electronic polarizability α is defined by the coefficient in a power series

$$W = W_0 - (\alpha_z/2)E^2 + \cdots \quad (10')$$

Then substitution of (9') in (7) gives

$$\alpha_z = (4/a_0)(\langle zg\rangle - \langle z\rangle\langle g\rangle)^2/\langle(\nabla g)^2 + (\nabla h)^2\rangle \quad (11c)$$

where a_0 is the Bohr radius. For minimum W (10'), function h is made equal to zero. Function g is assumed to have a form analogous to (12)

$$g = ax + by + cz \quad (12')$$

Substitution of (12') in (11c) and determination of the ratio $a:b:c$ for the minimum energy (10') gives

$$a:b:c = (\langle xz\rangle - \langle x\rangle\langle z\rangle):(\langle yz\rangle - \langle y\rangle\langle z\rangle):(\langle z^2\rangle - \langle z\rangle^2) \quad (13')$$

By substituting (12') and (13') in (11c) and taking the sum of the values for all the electrons, one obtains the molecular electronic polarizability

$$\alpha_z = (4/a_0)\sum_i [(\langle x_iz_i\rangle - \langle x_i\rangle\langle z_i\rangle)^2 + (\langle y_iz\rangle - \langle y_i\rangle\langle z_i\rangle)^2 + (\langle z_i^2\rangle - \langle z_i\rangle^2)^2] \quad (14c)$$

The mean value of α is given by

$$\alpha_{av} = (\alpha_x + \alpha_y + \alpha_z)/3 = (4/3a_0)\sum_i [(\langle x_i^2\rangle - \langle x_i\rangle^2)^2 + (\langle y_i^2\rangle - \langle y_i\rangle^2)^2 + (\langle z_i^2\rangle - \langle z_i\rangle^2)^2 + 2(\langle x_iy_i\rangle - \langle x_i\rangle\langle y_i\rangle)^2 + 2(\langle y_iz_i\rangle - \langle y_i\rangle\langle z_i\rangle)^2 + 2(\langle z_ix_i\rangle - \langle z_i\rangle\langle x_i\rangle)^2] \quad (15c)$$

Equations 14c and 15c are independent of the choice of the origin. For atoms, eq. 15c gives the well known formula

$$\alpha_{av} = (4/9a_0)\sum_i \langle r_i^2\rangle^2$$

NAGOYA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Dipole Moments and Optical Dispersion of Perchloro-fluorobutanes, Butadienes, Butenes and Propylenes[1]

BY EMILE RUTNER AND S. H. BAUER

RECEIVED MAY 4, 1959

Dipole moments and refractive indices between 4358 and 6565 Å. were measured for a series of perchloro-fluorobutanes, butadienes, butenes and propylenes. The optical dispersion was found to obey the relation $(n_\lambda^2 + 2)/(n_\lambda^2 - 1) = a + c_i[1/\lambda^2 - 1/\lambda_i^2]$, where λ_i is a "characteristic frequency," and a and c_i are constants characteristic of the substance. From the increments in refractivities for the substitution of F for Cl for a series of fluorocarbons, a consistent set of bond refractivities was deduced for the CF bond (1.75 cc.) and for the CCl bond (6.48 cc.) in a perhalogenated environment. Similarly, by using the increment of dipole moment for the substitution of F for Cl (0.5 D) in a perhalogenated environment and a value of μ (1.05 D) for the CCl bond moment, the minimum, maximum and free rotation dipole moments for the series of perhalocarbons studied were calculated and related to the measured dipole moments. The barrier height hindering free rotation in $CF_2{=}CCl{-}CCl{=}CF_2$ was estimated from the measured dipole moment (0.35 D).

Data on the optical dispersions and dipole moments of perhalogenated butanes, butenes and butadienes have not as yet been reported. A study of these molecular properties of perchloro-fluorobutanes, butenes, butadienes and propylenes was undertaken with the expectation of relating the evident trends in these properties to the corresponding changes in molecular structures.

(1) Part of the Ph.D. Thesis, submitted by E. Rutner, to the Faculty of the Graduate School, Cornell University, June, 1951.

Experimental

Materials.—The synthesis and purification of some of the compounds used will be described elsewhere[2]; herein we have

(2) W. T. Miller and E. Rutner (to be published).

TABLE I

REFRACTIVE INDICES, $n^{20}\lambda$, OF SOME PERCHLOROFLUOROCARBONS BETWEEN 4358 AND 6565 Å.[a]

Compound	λ 6565	5893	$n^{20}\lambda$ 5770	5461	5016	4358 Å.
$CCl_3CCl{=}CCl_2$	1.5444	1.5487	1.5492	1.5522	1.5543	....
$CF_3CCl{=}CCl_2$	1.4070	1.4095	1.4105	1.4122	1.4139	1.4232
$CF_3CCl{=}CClCF_3$[b]	1.3455	1.3476	1.3486	1.3496	1.3522	1.3571
$CCl_2{=}CClCCl{=}CCl_2$	1.5504	1.5556	1.5566	1.5597	1.5636	....
$CClF{=}CClCCl{=}CClF$[b]	1.4720	1.4760	1.4767	1.4793	1.4826	1.4934
$CClF{=}CClCCl{=}CF_2$[b]	1.4282	1.4316	1.4324	1.4343	1.4371	1.4468
$CF_2{=}CClCCl{=}CF_2$	1.3811	1.3835	1.3840	1.3857	1.3874	1.3950
$CClF{=}CFCF{=}CClF$[b]	1.3979	1.4011	1.4017	1.4036	1.4066	1.4163
$CCl_2FCCl_2CCl_2CCl_2F$	1.5232	1.5261	1.5269	1.5285	1.5304	1.5387
$CClF_2CCl_2CCl_2CCl_2F$	1.4917	1.4941	1.4946	1.4959	1.4974	1.5050
$CClF_2CCl_2CCl_2CClF_2$	1.4584	1.4603	1.4611	1.4623	1.4635	1.4704
$CCl_2FCCl_2CCl_2CCl_2F$	1.4539	1.4560	1.4567	1.4578	1.4590	1.4650

[a] Measurements made at 20.00 ± 0.05°. Mixtures of isomers.

listed the estimated purities based on distillation and/or freezing point curves, given in parentheses after each compound. These other compounds will be described in the forthcoming publication[2]: $CCl_2FCCl_2CCl_2CCl_2F$ (>99.9), $CCl_2FCCl_2CCl_2CClF_2$ (>99.9), $CClF_2CCl_2CCl_2CClF_2$ (>99.0), $CClF{=}CClCCl{=}CClF$ (>99.0), $CClF{=}CClCCl{=}CF_2$ (>99.0), $CF_2{=}CClCCl{=}CF_2$ (>99.9). Additional compounds were supplied by the persons noted: A. H. Fainberg, $CCl_2{=}CClCCl_3$ (>99.5), $CCl_2{=}CClCF_3$ (>99.0); R. T. Carroll, $CCl_2FCClFCClFCCl_2F$ (>99.0), $CClF{=}CClFCClF{=}CClF$ (>99.0); F. W. McLafferty, a mixture of $CCl_2{=}CClCCl_2CCl_3$ and $CCl_3CCl{=}CClCCl_3$, n-C_4Cl_{10} (>99.0); W. E. Tait, $CF_3CCl_2CCl_2CF_3$ (>99.0), $CF_3CCl{=}CClCF_3$ (>99.0).

Two compounds were obtained from commercial sources. The fluorobenzene (Eastman Kodak Company, pure grade) was distilled through a 70 × 1.6 cm. packed column; the 50% center fraction had the physical properties listed: b.p. 84.6° (740 mm.), f.p. −41.7°, n^{20}_D 1.4677; Smakula[3] gives b.p. 85.0° (760 mm.), f.p. −41.9°, n^{20}_D 1.4677. Perchlorobutadiene was obtained from the Hooker Electrochemical Company and purified in the following manner. A 500-cc. sample was washed with four or five 50-cc. volumes of methyl alcohol or until the yellow color had been extracted. The sample was then stirred for 2 hr. with sulfuric acid, washed with distilled water until neutral and filtered through a 3″ column of P_2O_5. Finally, it was distilled through a 50 × 3.0 cm. packed column at 100 mm. pressure. The fraction containing 10% of the material after 80% had been distilled gave a cooling curve indicating that it was 99.9% pure. The physical properties of this fraction were: b.p. 144.1° (100 mm.), f.p. −18.6°, n^{20}_D 1.5557, d^{20}_4 1.6794; Kohlrausch and Wittek[4] gave b.p. 210-212° (760 mm.), f.p. −15°, n^{20}_D 1.5556.

The solvents used were carefully purified; cyclohexane, according to the technique described by Bruun and Hicks-Bruun,[5] had these physical properties: f.p. 6.5 ± 0.1°, n^{20}_D 1.4262, d^{20}_4 0.7785; the literature[6] gives f.p. 6.554°, n^{20}_D 1.4263, d^{20}_4 0.7785. Benzene, Baker and Adamson reagent grade, was distilled in the presence of sodium. The fraction used had: n^{20}_D 1.5010, d^{20}_4 0.8787; the literature[6] gives n^{20}_D 1.5010, d^{20}_4 0.8789.

Handling of Samples.—Since the perhalogenated butadienes are readily oxidized, precautions were taken to minimize exposure to the atmosphere. Into a number of prepared flasks, about 100 g. of the butadienes was distilled under a nitrogen blanket; the flasks were sealed. These were later attached to a manifold containing a plug of Ascarite and Dehydrite; attached also were several pear-shaped flasks with small glass bulbs which had been weighed. The manifold was evacuated; the sample was distilled back and forth over the Ascarite several times and finally condensed into the pear-shaped flasks; nitrogen was admitted to the manifold to force the butadiene into the small bulbs. The manifold then was dismounted, the bulbs sealed and weighed.

(3) A. Smakula, *Z. ang. Chem.*, **47**, 657 (1943).

(4) K. W. F. Kohlrausch and R. Wittek, *Ber.*, **75**, [3] 227 (1942).

(5) J. H. Bruun and M. M. Hicks-Bruun, *J. Research Natl. Bur. Standards*, (R. P. 360), **7**, 607 (1931).

(6) "Selected Values of Physical Properties of Hydrocarbons," U. S. Dept. of Commerce, Natl. Bur. Stds., Washington, D. C.

Refractive index measurements were made with a Pulfrich refractometer; the cell was sealed to the prism by means of fish glue which had been treated according to the formula given by Strong.[7] The samples were either poured or distilled into the cell which was covered by a condenser.

The light sources used were: (a) a sodium lamp, (b) a hydrogen discharge tube and (c) a mercury lamp. The desired lines were selected by means of filters: 6565 Å. (b), 5893 Å. (a), 5770 Å. (c), 5016 Å. (b), and 4358 Å. (c). The prisms were calibrated at each wave length using the data given by Lowry and Alsopp.[8] All measurements shown in Table I were made at 20 ± 0.05° and are probably accurate to ± 0.00015.

Dielectric constants were measured in the apparatus described by Keenan.[9] In essence, it was a capacitance bridge operating as heterodyne beat oscillator, with a crystal control section oscillating at 1.57 megacycles; readings were taken on a vernier dial capacitor in parallel with the measuring cell. The apparatus was standardized with benzene and its accuracy checked with cyclohexane. The dielectric constant of benzene was taken as 2.283 at 20° and of cyclohexane as 2.027[10] at the same temperature. The accuracy of the dielectric constants was estimated to be ± 0.002 on the basis of the data obtained for cyclohexane.

The cell used consisted of three concentric gold-plated brass cylinders similar to that described by Smyth.[11] The first and third cylinders were grounded while the center one was suspended on Kel-F buttons, thus forming two condensers in parallel. The cell capacity filled with air was 38 μμf. and its volume 15 ml. The temperature of the cell was maintained at 20.0 ± 0.15° by means of an oil-bath.

Treatment of the Data

Dispersion Data.—The data for each compound shown in Tables I and II were reduced using the relations[10,12]

$$(P_E)_\lambda = \phi_\lambda(M/d) = [(n_\lambda^2 - 1)/(n_\lambda^2 + 2)](M/d) \quad (1)$$

$$1/\phi_\lambda = c_i[(1/\lambda^2) - (1/\lambda_i^2)] = a + (c_i/\lambda^2) \quad (2)$$

Subscript λ designates the wave length at which the measurement was made; P_E is the electronic polarization; n, the refractive index; M, the molecular weight; and d, the density. A plot of $1/\phi_\lambda$ was found to be linear with $1/\lambda^2$ for most of the compounds, over the region 4358 to 6565 Å.;

(7) J. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1947.

(8) T. M. Lowry and C. C. Alsopp, *Proc. Roy. Soc. (London)*, **A133**, 54 (1931).

(9) V. J. Keenan, Ph.D. Thesis, Cornell University, 1942.

(10) C. P. Smyth and W. M. Stoops, THIS JOURNAL, **51**, 3319 (1929).

(11) C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalogue Company, Reinhold Publ. Corp., New York, N. Y., 1931.

(12) N. Bauer, "Physical Methods in Organic Chemistry," Vol. I, Chap. 20, Ed. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1949.

TABLE II

OPTICAL DISPERSION OF SOME PERHALOCARBONS[a]

Compound	a	$c_i \times 10^{10}$	λ_i (Å.)
$CCl_2FCCl_2CCl_2CCl_2F$	3.335	2.70	900
$CClF_2CCl_2CCl_2CCl_2F$	3.506	2.47	840
$CClF_2CCl_2CCl_2CClF_2$	3.722	2.58	835
$CCl_2FCClFCClFCCl_2F$	3.749	2.70	850
$CCl_2{=}CClCCl{=}CCl_2$	3.235	4.19	1142
$CClF{=}CClCCl{=}CClF$	3.688	4.90	1166
$CF_2{=}CClCCl{=}CClF$	3.999	4.94	1112
$CF_2{=}CClCCl{=}CF_2$	4.144	4.66	1062
$CClF{=}CFCF{=}CClF$	4.255	4.84	1068
$CF_3CCl{=}CClCF_3$	4.812	4.74	994
$CCl_2{=}CClCCl_3$	3.233	2.93	952
$CCl_2{=}CClCF_3$	4.150	3.76	952

[a] Constants for equation 2; *i.e.*, $1/\phi_\lambda = a - c_i/\lambda^2$. c_i is then the slope of the plot and the intercept for $\lambda = \infty$, $1/\phi_\infty = a$.

thus, λ_i was evaluated from the intercept extrapolated to $1/\lambda^2 \rightarrow 0$. The values of P_E^∞ and P_E^D, *i.e.*, $\lambda \rightarrow \infty$, and $\lambda = Na_D$ were subsequently used in estimating the dipole moments. Values of P_E for the solid compounds were obtained from polarization measurements of benzene solutions of the compounds, assuming that the molecular polarizations of the solvent and solute were additive. The refractive indices of benzene were taken from reference 8. The significant deviations of the P_E^D values deduced for the solid compounds from those calculated assuming bond additivity probably are due to the departure from strict additivity of the solute and solvent polarizabilities.

Polarization Data.—Dielectric constants of solutions of the compounds in cyclohexane and in benzene were measured and used in evaluating dipole moments of the solutes by means of the relations[11]

$$P_{12} = P_1c_1 + P_2c_2 = [(\epsilon - 1)/(\epsilon + 2)](M/d) \quad (3)$$
$$P = P_A + P_E + P_\mu \quad (4)$$

where P is the polarization; c, the concentration in mole fraction; ϵ, the static dielectric constant. The subscripts, 1, 2 and 12, refer to the solvent, solute and solution, respectively, while P_A, P_E and P_μ designate the contribution to P of the atomic, electronic and dipole orientation polarizations, respectively. In equation 3, the value of P_2 used was $({}_\infty P_2)$, that obtained by extrapolating P_2 *vs.* c_2 to infinite dilution, while $(P_E)_2$ was evaluated from equation 1, using either ϕ_∞ or ϕ_D. $(P_A)_2$ was estimated on the assumption that it was an additive bond property, as proposed by Sutton[13] and LeFèvre[14] for certain cases. The additivity of P_A was tested utilizing the values given in Table III. Since P_A is to be characteristic of a bond or atomic grouping, its value for decachlorobutane should be 2.5 times that for carbon tetrachloride, or 5 to 7.5 cc.; the value found from the relation ($P_A = P - P_E^\infty$) was 5 ± 2.5 cc.; this agreement is within experimental error. The dipole moments listed in Table IV then were obtained (at 20°) using either (a)

(13) L. E. Sutton and I. E. Coop, *J. Chem. Soc.*, 1283 (1938).

(14) R. J. W. LeFèvre and D. A. A. S. Narayana Rao, *Australian J. Chem.*, **7**, 135 (1954).

TABLE III

ATOMIC POLARIZATION OF SOME PERHALOGENATED COMPOUNDS

Compound	P_A (cm.)[3]
CF_4	2.86
CCl_4	2 to 3
CCl_3F	3.0
CCl_2F_2	4.1
CCl bond	0.5
CF bond	0.7
C_2Cl_4	2.8

$\mu_\infty = 0.0127(P - P_A - P_E^\infty)_2$ or (b) $\mu_D = 0.0127(P - P_E^D)_2$ wherein $(P_A)_2$ was negligible.

In two separate experiments, a check was made on the procedure outlined above; these gave for μ_D for fluorobenzene: 1.45 and 1.52 *D;* Wesson[15] gives 1.45 and 1.58 *D*. The probable errors in the calculated quantities given in Tables II and IV are: $a \pm 0.005$, $\phi \pm 0.0005$, $c_i \pm 0.015$, $P \pm 2.5$ cc., and $\mu \pm 0.1\,D$ if $\mu > 1\,D$ and $\pm 0.3\,D$ if $P_\mu < 5$ cc.

Discussion

The *optical dispersion* may be expressed by the equation[12,16]

$$\phi_\lambda = [(n_\lambda^2 - 1)/(n_\lambda^2 + 2)] = \sum_j f_{ij}/(\nu_{ij}^2 - \nu^2) \quad (5)$$

where ϕ_λ, n_λ and λ are defined above; ν_{ij} represents the characteristic frequencies for absorption, for the molecule making a transition between the states i and j; f_{ij} is the corresponding "oscillator strength." If one selects a single term only from the sum in (5), he will obtain the dominant ν_{ij} or the corresponding λ_i as used in (2). The values of λ_i thus deduced are listed in Table II. The corresponding energies are in the far ultraviolet and are larger than those found for the ionization potentials (i.p.) of most organic compounds; typical values for halogenated compounds cited by Price,[17] Walsh[18] and Sugden[19] correspond to transitions in the 1300 to 1500 Å. region. Since an i.p. measures a limiting R ← N transition (Normal state of molecule → Rydberg type electronically excited state) and λ_i represents a hypothetical R ← N transition, one might expect that the energies of both will follow an order for the perhalocarbons similar to that for the partially chlorinated hydrocarbons. The order for the latter, with typical values of their i.p., is: (a) saturated compound, C_2H_5Cl, 10.89 e.v., (b) vinyl compound, C_2H_3Cl, 10.0 e.v., and (c) conjugated diene, chloroprene, 8.93 e.v.[17] The justification for this sequence of the magnitudes of i.p. or in general for an energy interval in the R ← N transitions of any similar series of compounds is given by Coulson[20] and Price.[17] An increase in the ionic character of a bond or molecule lowers the energy of the ground state of the ion and, con-

(15) L. G. Wesson, "Table of Dipole Moments," Laboratory for Insulator Research, Massachusetts Institute of Technology, Cambridge, Mass.

(16) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944.

(17) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(18) A. D. Walsh, *Trans. Faraday Soc.*, **41**, 35 (1945).

(19) T. M. Sugden and A. D. Walsh, *ibid.*, **41**, 76 (1945).

(20) C. A. Coulson, "Valence," Oxford University Press, London, 1952, p. 186.

TABLE IV

POLARIZATION AND DIPOLE MOMENTS OF SOME PERCHLOROFLUOROCARBONS

	Polarization, cc.					Dipole moments, Debye's[b]				
						Obsd.		Calcd.		
Compound	Calcd.[a] (P_E^D)	$(P_E^D)_2$	$(P_E^\infty)_2$	$_\infty P_2$	Calcd. P_A	μ_D	μ_∞	μ_{max}	μ_{min}	μ_{FR}
$CCl_3CCl_2CCl_2CCl_3$	68.69	71.6 B	69.0 B	77.0 B	5.0 ± 2.5	0.5	0.38	Assumed 0.0		
$CCl_2FCCl_2CCl_2CCl_2F$	59.37	58.89 59.7 C	57.43	76.4 C 77.3 B	7.0	.91 C .93 B	.75 C .78 B	1.67	0.0	1.00
$CCl_2FCCl_2CCl_2CClF_2$	54.71	54.23 54.6 C	52.52	76.9 77.5 C	8.1	1.03 B 1.05 C	.88 B .89 C	1.70	.14	1.09
$CClF_2CCl_2CCl_2CClF_2$	50.05	49.59 50.3 C	48.59	76.0 B 74.6 C	7.0	1.12 B 1.09 C	.98 B .95 C	1.80	.0	1.28
$CCl_2FCClFCClFCCl_2F$	50.05	49.82 50.0 C 49.8 B	48.87	70.5 C 71.0 B	9.0	1.00 B 0.99 C	.79 B .76 C	1.64	.0	1.17
$CF_3CCl_2CCl_2CF_3$	40.73	40.2 B	39.4 B	59.9 B 58.4 C	11.2	.93 C .96 B	.60 C .66 B	1.38	.0	1.00
$CCl_2{=}CClCCl{=}CCl_2$	49.32	50.00 49.9 B	48.10	53.8 B	4.5 ± 2.5	.4 B	.2	Assumed 0.0		
$CClF{=}CClCCl{=}CClF$	40.00	39.99 39.8 B	38.42	65.5 B	4.5	1.11 B	1.02 B	0.0 *trans–trans* .95 .7 *cis–cis*	 0.0	 0.73 *cis–trans*
$CF_2{=}CClCCl{=}CClF$	35.34	34.85 33.6 B	33.11	36.0 B	4.5	0.28 B	0.0 B	1.06 0.5 *trans*	0.5	0.82 *cis*
$CF_2{=}CClCCl{=}CF_2$	30.68	29.73 29.5 B	28.80	36.2 B	4.5	0.55 B	0.37 B	.94	0.0	0.67
$CClF{=}CFCF{=}CClF$	30.68	30.38 29.5 B	29.46	55.7 B	4.5	1.09 B	1.01 B	.94 1.15 *cis–trans* 0.0 *trans–trans*	0.0	0.68 *cis–cis*
$CF_3CCl{=}CClCF_3$	30.63	30.75 31.1 B	29.88	43.1 B	6.5	0.71 B	0.53 B	1.40 *cis* 0.0 *trans*		
$CCl_3CCl{=}CClCCl_3$	58.62	58.52 58.2 B	56.0 B	65.2 B	6.0	.58 B	.38 B	.58 *cis* .0 *trans*		
$CCl_2{=}CClCCl_3$	44.34	44.88	43.66	53.6	4.5	.64 B	.46 B			
$CCl_2{=}CClCF_3$	30.36	30.74 B 30.52	29.76	58.3 B	4.5	1.18 B	1.07 B			

[a] Calcd. (P_E^D) was obtained by using the following bond refractivities: CF, 1.82; CCl, 6.48; C=C, 4.16; C–C, 1.296; C–C between two double bonds, 2.12; CH, 1.674 (see text for source). [b] B and C refer to measurements in benzene and cyclohexane, respectively. For the dipole moments which were calculated, the symbols employed were: μ_{max}, maximum dipole moment; μ_{min}, minimum dipole moment; μ_{FR} is the free rotation moment. Where no μ_{FR} is indicated, μ is independent of the angle of rotation. Where a particular isomer (*i.e.*, *cis–cis*, etc.) is indicated, the calculated moments are for that particular stereoisomer.

sequently, that of the R states of the molecule more than the N state of the molecule. The i.p. and $1/\lambda_i$ should, therefore, shift to lower energies with an increase in ionic character of the molecule.

The dispersion data offer some information on the refractivities which may be assigned to individual bonds in the various compounds. Some of the conclusions which were drawn have already been anticipated in a forthcoming publication by Fainberg and Miller,[21] so that our results complement theirs. Fainberg and Miller[21] have shown by analysis of the P_E^D of MR_D values of an extensive series of compounds that a consistent set of atomic refractivities, AR_D, for perhalogenated hydrocarbons may be obtained. The best values they deduced are: C, 2.584, F, 1.165 and H, 1.029; however, one must assign values to the refractivities of the other halogens depending on their position on the carbon skeleton; they tabulated corrections for the variations in AR_D with structure. The data cited in Tables V and VI indicate that the conclusions of Fainberg and Miller[21] can be substantiated by evaluating the increment in P_E^D upon substitution of Cl for H, or F for Cl, *i.e.*, $[P_{Cl} - P_H]$ or $[P_F - P_{Cl}]$. The increment in refractivity is a more reliable indication of the effect of substitution on bond refractivity than P_E^D itself, because it does not depend on an arbitrary choice of individual AR_D. As shown in Table V, the values $[P_{Cl} - P_H]$ do vary significantly with atomic grouping in the molecule, while values of $[P_{Cl} - P_F]$ are suitably constant for substitution in perhalogenated propanes and butanes, Table VI. The only significant difference appears for $CCl_3CClFCCl_2F$ and cannot be explained in terms of a structural factor.

In the case of unsaturated compounds, the exaltation in P_E^D is associated with variation in the contribution of the V ← N transition due to the shift in $\lambda(V_1 \leftarrow N)$. This contribution can be evaluated from (5), by using only the term involving $\lambda_1 = (V_1 \rightarrow N)$[22] and defining the exaltation as $\Delta P_E^D = [P_E^D - (P_E^D)_c]$, where $(P_E^D)_c$ is obtained by using the values for the bond refractivities given in Table IV. One may write for $\Delta P_E^D = c^2[f_{ij}/(1/\lambda_i^2 - 1/\lambda^2) - f_{ijc}\,(1/\lambda_{ic}^2 - 1/\lambda^2)]$, where the term with subscript c refers to a regular double bond and the other term to the molecule in question. A plot of ΔP_E^D *vs.* $1/\lambda_i^2$ should be roughly linear if the f_{ij}'s are approximately equal. Figure 1 shows this relation for the λ ($V_1 \leftarrow N$) transition in the s-*cis* form of the perchlorofluorobutadienes. Added to the plot are data for butadiene and chloroprene; the large departure of these points from the curve can in part be attrib-

(21) A. H. Fainberg and W. T. Miller (to be published).

(22) R. S. Mulliken and C. A. Rieke, *Ann. Repts. Prog. Phys.*, **8**, 231 (1941).

TABLE V

ELECTRONIC POLARIZATIONS FOR THE SODIUM-D LINE OF SOME HYDROCARBONS AND THEIR HALIDES

Compound	P_E^D, cc.	ΔP_E^D, cc.[a]
C_2Cl_4	30.33	4.95
C_2HCl_3	25.38	
n-$C_5H_{11}Cl$	30.02	4.75
n-C_5H_{12}	25.271	
$(CH_3)_2CCl(C_2H_5)$	30.16	4.86
$(CH_3)CH(C_2H_5)$	25.302	
n-$C_6H_{13}Cl$	34.67	4.75
n-C_6H_{14}	29.918	
n-$C_7H_{13}Cl$	39.33	4.77
n-C_7H_{14}	34.557	
n-$C_8H_{17}Cl$	43.93	4.74
n-C_8H_{18}	39.191	4.98
$(CH_3)CHCl(C_6H_{13})$	44.17	
n-$C_{16}H_{33}Cl$	80.93	4.58
n-$C_{16}H_{34}$	76.354	
CCl_4	26.47	5.11
$CHCl_3$	21.36	5.07
CH_2Cl_2	16.29	
C_2H_5Cl	35.57	4.95
$CHCl_2CHCl_2$	30.62	4.75
$CHCl_2CH_2Cl$	25.87	4.80
CH_2ClCH_2Cl	21.07	
$CH_2ClCHClCH_2Cl$	30.37	4.85
$CH_2ClCH_2CH_2Cl$	25.52	4.58
n-C_3H_7Cl	20.94	
$CH_2Cl(CH_2)_2CH_2Cl$	30.20	4.78
n-C_4H_9Cl	25.42	

[a] ΔP_E^D represents the difference in refractivity between a carbon–chlorine bond and a carbon–hydrogen bond. The values for the carbon–hydrogen bond used were 1.674, and for the carbon–carbon bond, 1.296. Since the average ΔP_E^D of the saturated compounds was 4.81, the carbon–chlorine bond refractivity used was 6.48.

TABLE VI

ELECTRONIC POLARIZATION FOR THE SODIUM-D LINE OF SOME CHLOROFLUOROPROPANES

Compound	P_E^D, cc.	ΔP_E^D, cc.[a]
$CCl_3CF_2CCl_3$	45.13	4.62
$CCl_3CF_2CCl_2F$	40.51	4.68
$CCl_2FCF_2CCl_2F$	35.83	4.68
$CCl_2FCF_2CClF_2$	31.15	4.69
$CClF_2CF_2CClF_2$	26.46	
$CCl_3CClFCCl_3$	49.76	4.66
$CCl_3CClFCCl_2F$	45.10	4.81
$CCl_2FCClFCCl_2F$	40.29	4.68
$CCl_2FCClFCClF_2$	35.61	4.72
$CClF_2CClFCClF_2$	30.89	4.64
$CClF_2CClFCF_3$	26.25	

[a] ΔP_E^D represents the difference in the bond refractivities of carbon–chlorine and carbon–fluorine bonds. Using the value obtained in Table V for the carbon–chlorine bond refractivity, an average value of 1.75 was obtained for the carbon–fluorine bond refractivity.

uted to the poor development of the s-*cis* band, making it difficult to identify the maximum wave length of absorption.

Dipole moments were obtained by reducing the polarization data as given above. A comparison then was made between the observed dipole moments (μ_{obs}) and those calculated by assuming a consistent set of values for the CCl and CF bond moments, although these do depend on the molecular environment of the particular CF and CCl bonds, Table IV. For example, an estimate of $\Delta\mu$(CF–CCl) can be obtained either directly from the dipole moments of CCl_3F (0.48 D)[15] and of CF_3CCl_2F (0.53 D)[15] or from the difference between the dipole moments of CCl_3H (1.05 D)[15] and CF_3H (1.59 D).[15] A reasonable value is $\Delta\mu$(CF–CCl) = 0.5 D in a perhalogenated environment. In contrast an estimate of $\Delta\mu$ derived from the difference between CH_3F (1.81 D)[15] and CH_3Cl (1.86 D),[15] in a non-perhalogenated environment, is at most 0.1 D. The corresponding value used for the CCl bond was that of CCl_3H[15] or 1.05 D. A test of the above assumptions was made by calculating μ for $CClF_2CCl_2F$ from the polarization data given by Fuoss[23]: P = 34.5 cc. Using a value of P_A = 6.5 cc. (that of C_2F_6) and P_E = 21.5 cc., calculated from bond refractivites, a value of P_μ = 5.58 cc. or μ = 0.53 D was obtained. Fuoss assumed that this molecule had a zero dipole moment, on the basis of the dipole moments of CH_3F and CH_3Cl given above. Maximum, minimum and free rotation values of the dipole moment were also calculated and found to be 0.94, 0.0 and 0.68 D, respectively. A value of $\Delta\mu$(CCl–CF) = 0.5 D is in agreement with μ = 0.52 D reported for C_2F_5Cl by Di Giacomo and Smyth.[24]

The calculation of dipole moments of molecules from assigned bond moments on the assumption of specified configurations has been discussed by many investigators.[25–27] For the perhalogenated butanes, the calculation was carried out as indicated. Values of $\Delta\mu$(CCl–CF) = 0.5 D and μ(CCl) = 1.05 D were assumed. The butane skeleton which may be represented as

```
C—C
1  2\
     C—C
     3  4
```

permits rotation around three bonds: (a) group 1, with respect to 2, (b) group 4, with respect to 3, and (c) groups 1 and 2 together, with respect to 3 and 4 together. The molecule was considered to be split into two ethyl fragments; the dipole moments for free rotation of group 1, with respect to 2, and that of 4, with respect to 3, were calculated by resolving the moments of each group and assuming that the resultant moments rotated freely with respect to each other. Then these resultants were assumed to rotate freely with respect to each other around the 2,3 C–C bond. The minimum and maximum moments of the butanes reported were those corresponding to the minimum and maximum moments of the free rotation moments of the ethyl fragments. All bond angles were assumed to be tetrahedral.

All the butanes studied had dipole moments which were less than those expected for free rotation. This fact can be explained by assuming restricted rotation around each of the CC bonds,

(23) R. Fuoss, THIS JOURNAL, **60**, 1633 (1938).
(24) A. Di Giacomo and C. P. Smyth, *ibid.*, **77**, 774 (1955).
(25) L. Meyer, *Z. physik. Chem.*, **B8**, 27 (1930).
(26) J. W. Williams, *ibid.*, **A138**, 75 (1928).
(27) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

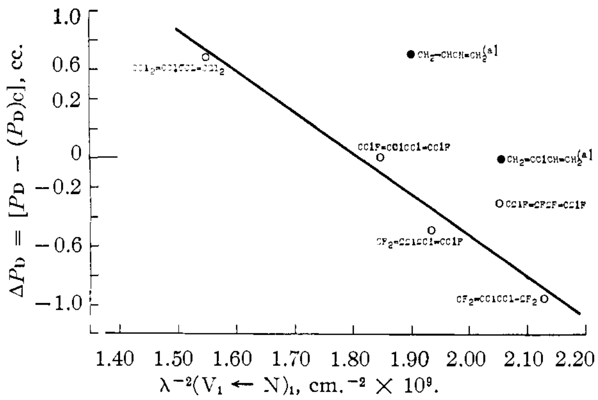

Fig. 1.—The variation of the exaltation of molar refractivities with $\lambda_i^{-2} = \lambda^{-2}(V_1 \leftarrow N)$[29] for the s-*cis* form of some perchlorofluoro-1,3-butadienes: (a) butadiene, P_D 21.1,[30] $(V_1 \leftarrow N)$[30] 2288 Å.; chloroprene, P_D 25.31,[31] $(V_1 \leftarrow N)$ 2216 Å.[32]

since the free rotation dipole moments essentially measure the molecular moment when the dipoles are 90° to each other; a dipole moment of less than this indicates restricted rotation with the molecule in the s-*trans* configuration.

In Table IV, there are also data for perhalogenated propylenes, butenes and butadienes. The propylenes and butenes which were studied were treated as substituted ethylenes, since all the compounds used had either a Cl, CCl_3 or CF_3 group attached to a vinyl carbon atom. The moment of $CCl_3CCl{=}CCl_2$, $\mu = 0.45$ *D*, is the difference in the dipole moments between a CCl_3 group and a Cl atom attached to a perchlorinated vinyl radical. A corresponding difference $\mu(CF-CCl)$ attached to a vinyl carbon is given by the dipole moment of $CCl_2{=}CClF$, (ref. 27, p. 276) 0.4 *D*. This is in agreement with the value used in calculating the results in Table IV.

That the dipole moment of $CF_3CCl{=}Cl_2$, 1.07 *D*, is a direct measure of the difference $\Delta\mu(CF_3\text{–}CCl)$ between the moment of a CF_3 and Cl atom attached to a perchlorinated vinyl group is of special interest. The butenes reported in Table IV were mixtures of *cis–trans* isomers; hence, the observed moments gave some indication of the isomeric composition. For example, the observed moment of octachlorobutene, 0.39 *D*, indicates that the sample used was a mixture of *cis–trans* butene-2 and of butene-1. The sample of $CF_3CCl{=}CClCF_3$ used was a mixture of *cis-trans* isomers, and the dipole moment indicated that the probable composition of the mixture was 50% *cis* and 50% *trans*.

The data given in Table IV for the perhalogenated butadienes can be related to the composition of the samples used and to their molecular configurations. Suppose we accept the value of $P_\mu = 0$ for $CCl_2{=}CClCCl{=}CCl_2$; then $P_A = 5.0$ cc., as noted in Table IV, is obtained; this was

(28) J. G. Aston, H. W. Wooley, G. J. Szasz and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 645 (1946).

(29) S. H. Bauer and E. Rutner (to be published).

(30) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publ. Corp., New York, N. Y., 1939.

(31) N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 1005 (1946).

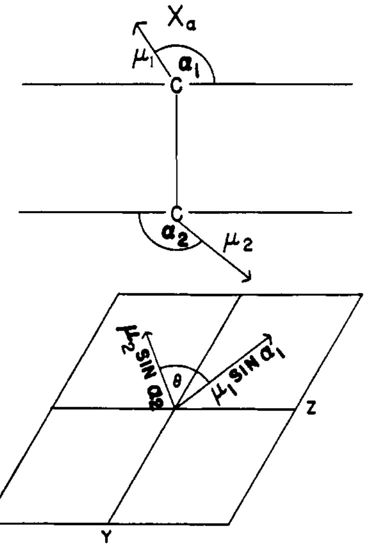

Fig. 2.—The spatial relation between two dipoles with partial free rotation; α is the angle between the dipole and the x–y plane, and θ is the angle between two dipole rotating with respect to each other.

then used in estimating the moments of other perhalogenated butadienes. The measured moment (1.02 *D*) for $CFCl{=}CClCCl{=}CClF$ appears anomalous because the sample was a mixture of isomers and should have had a moment less than the estimated maximum, 0.95 *D*. In contrast, the observed moment of $CF_2{=}CClCCl{=}CFCl$ (0.0 *D*) indicates that it was predominantly a *trans* isomer, while that of $CClF{=}CFCF{=}CClF$ (1.0 *D*) indicates that it is predominantly a mixture of *cis–cis* and *trans–trans* isomers.

The measured dipole moment of $CF_2{=}CClCCl{=}CF_2$ (0.37 *D*) provided an opportunity to estimate the potential barrier restricting rotation about the single bond in this molecule; *i.e.*, the interconversion of the s-*trans*, C=C–C=C, and s-*cis*, C=C–C=C, forms.

If a potential function restricting rotation is assumed similar to that postulated by Aston,[28] *et al.*, for butadiene, in accounting for their thermodynamic data

$$V = V_0/2[1 - \cos 2(\theta - \pi)] \text{ for } \pi/2 \leqslant \theta \leqslant \pi \quad (6a)$$

$$V = V_0/2 + V_0/4[1 - \cos 2\theta] \text{ for } 0 \leqslant \theta \leqslant \pi/2 \quad (6b)$$

then V_0 may be estimated from the measured dipole moment of the perhalobutadiene. θ is defined as the angle between the two planes, each containing one of the resultant moments of a vinyl group and the common axis of rotation, Fig. 2. The resultant moment of each half of the molecule is 0.5 *D*, and each makes an angle $\alpha_1 = \alpha_2 = 109°$ with the axis of rotation. The square of the total dipole moment is given by

$$\mu^2 = A + B \cos \theta \quad (7)$$

If μ_1 and μ_2 were two unequal dipoles rotating with respect to each other

$$A = \mu_1^2 + \mu_2^2 - 2\,\mu_1\,\mu_2 \cos \alpha_1 \cos \alpha_2 \quad (8a)$$

$$B = 2\,\mu_1\,\mu_2 \sin \alpha_1 \sin \alpha_2 \quad (8b)$$

(32) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A174**, 220 (1940).

For the case considered, $\alpha_1 = \alpha_2 = 109°$, $B = A = (16/9)\ \mu^2$, and the average of the square of the dipole moment is

$$\overline{\mu^2} = \frac{\int_0^\pi \mu^2(\theta) \exp[-V(\theta)/RT]d\theta}{\int_0^\pi \exp[-V(\theta)/RT]d\theta} \qquad (9)$$

Substitute into (7)

$$\overline{\mu^2} = A + Bf$$

$$f = \frac{\int_0^\pi \cos\theta \exp[-V(\theta)/RT]d\theta}{\int_0^\pi \exp[-V(\theta)/RT]d\theta} \qquad (10)$$

Evaluation of (8) and substitution into (10) gave $B = A = 0.44$, $f = 0.69$. With $a = (V_0/2RT)$ and $T = 293°$K.

$$0.69 = \frac{e^{-a/2}\int_0^{\pi/2} \exp[(a/2)\cos 2\theta] \cos\theta\, d\theta + \int_{\pi/2}^{\pi} \exp[a \cos 2(\theta - \pi)] \cos\theta\, d\theta}{e^{-a/2}\int_0^{\pi/2} \exp[(a/2)\cos 2\theta] d\theta + \int_{\pi/2}^{\pi} \exp[a \cos 2(\theta - \pi)] d\theta} \qquad (11)$$

The integrals in (11) were evaluated graphically, giving $a = 2.56$, $V_0 = 3$ kcal., the depth of the s-*trans* barrier; *i.e.*, the magnitude of V for $\theta = \pi/2$. The s-*cis* barrier was assumed to be $V_0/2$ or 1.5 kcal.; *i.e.*, the magnitude of V for $\theta = \pi$. The value of V_0 thus obtained is less than that for butadiene,[28] which was 5 kcal., although it is expected to be larger due to the enhanced interaction between halogen atoms as contrasted to the hydrogen atoms.

The ratio of the number of molecules in the *trans* configuration to those in the *cis* configuration is given by $N_{trans}/N_{cis} = \exp(-a) = 12.9$, while the ratio of the number of molecules N_t/N_c, with θ in the interval $0 \leqslant \theta \leqslant \pi/2$, to those with θ in the interval $\pi/2 \leqslant \theta \leqslant \pi$ is given by

$$N_t/N_c = \frac{\int_0^{\pi/2} \exp[a \cos 2(\theta - \pi)]d\theta}{e^{-a/2}\int_{\pi/2}^{\pi} \exp[(a/2) \cos 2\theta]\, d\theta} = 7.8 \qquad (12)$$

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ITHACA, NEW YORK

[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Thermodynamics of Aqueous Ferricyanide, Ferrocyanide and Cobalticyanide Ions

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We have measured heats of solution of $K_3Fe(CN)_6$(c) and $K_3Co(CN)_6$(c) and the solubility of $K_3Co(CN)_6$(c) in water at 25°. The resulting data have been used in calculating that the standard partial molal entropies of $Fe(CN)_6^{-3}$ (aq) and $Co(CN)_6^{-3}$ (aq) are 63.4 and 55.7 cal./deg. mole, respectively. The heat of oxidation of $Fe(CN)_6^{-4}$(aq) by Br_2(liq) was measured and used with the above entropy of $Fe(CN)_6^{-3}$(aq) to obtain 17 cal./deg. mole for the standard partial molal entropy of $Fe(CN)_6^{-4}$(aq). The uncertainty in the entropy of $Fe(CN)_6^{-4}$(aq) is large, mainly because of the uncertainty of the oxidation potential used in the calculation. Heats of solution of $K_4Fe(CN)_6$(c) and $K_4Fe(CN)_6 \cdot 3H_2O$ (c) also were measured. The as yet undetermined Third Law entropies of $K_4Fe(CN)_6$(c) and $K_4Fe(CN)_6 \cdot 3H_2O$(c) can be combined with data now available to give a reliable thermodynamic value for the standard oxidation potential of the ferrocyanide-ferricyanide couple.

Stephenson and Morrow[2] have investigated the heat capacities of $K_3Fe(CN)_6$(c) and $K_3Co(CN)_6$(c) from 15 to 300°K. and have calculated entropies at 298.16°K. They used the standard entropy of $K_3Fe(CN)_6$(c) with thermodynamic data from the literature in calculating the standard partial molal entropy of $Fe(CN)_6^{-3}$(aq) and other derived thermodynamic quantities. They also pointed out the approximate nature of these derived quantities and suggested that careful determination of some heats of solution would be desirable.[3]

Heats of solution of $K_3Fe(CN)_6$(c), $K_4Fe(CN)_6$(c), $K_4Fe(CN)_6 \cdot 3H_2O$(c) and $K_3Co(CN)_6$(c) and the heat of oxidation of $Fe(CN)_6^{-4}$(aq) to $Fe(CN)_6^{-3}$(aq) by Br_2(liq) were measured. The solubility of $K_3Co(CN)_6$(c) in water at 25° was also determined.

(1) Alfred P. Sloan Research Fellow.

(2) C. C. Stephenson and J. C. Morrow, THIS JOURNAL, **78**, 275 (1956).

(3) We are grateful to Professor Morrow for calling this suggestion to our attention.

Experimental

The solution calorimeter used in this investigation has been described previously.[4,5] All of our heat determinations were at 25.0 ± 0.3° with 950 ml. of water or solution in the calorimeter.

Commercial C.P. $K_3Fe(CN)_6$(c) was purified according to the method of Stephenson and Morrow.[2] Baker "Purified" $K_4Fe(CN)_6 \cdot 3H_2O$(c) was recrystallized three times from distilled water. Aqueous solutions of $K_4Fe(CN)_6$ were never heated above 60°. Anhydrous $K_4Fe(CN)_6$(c) was obtained by drying the recrystallized trihydrate at 110° or by prolonged drying over P_2O_5 in a vacuum desiccator. No significant differences in analysis or heats of solution of $K_4Fe(CN)_6$(c) samples prepared in these two ways were noted.

Two samples of $K_4Fe(CN)_6 \cdot 3H_2O$(c) for heat of solution measurements were prepared. One sample was prepared by storing damp, recrystallized $K_4Fe(CN)_6 \cdot 3H_2O$(c) in a black-

(4) R. L. Graham and L. G. Hepler, THIS JOURNAL, **78**, 4846 (1956).

(5) C. N. Muldrow and L. G. Hepler, *ibid.*, **79**, 4045 (1957).