and Cu^{++}, −26.5 e.u.[2] the value $S^\circ_{Cu^+} = +8.3 \pm 2.0$ e.u. is found.

In view of the relation of Powell and Latimer[5] connecting the ionic radii and the partial molal entropies of aqueous ions this value seems more reasonable than the Bureau of Standards value.

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(5) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

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The "Carbonyl" Frequency in Polycyclic Quinones

BY D. HADŽI AND N. SHEPPARD

In a recent communication Josien and Fuson[1] have pointed out that the "carbonyl" frequency in some polycyclic compounds, mainly quinones, has an abnormally low value in the infrared spectrum (*e.g.*, 6.1 μ or approximately 1640 cm.$^{-1}$ for 3,8- and 3,10-pyrenequinone). In connection with some work on coking substances and coal extracts, we have also studied the infrared spectra of a series of polynuclear quinones and some related hydrocarbons. A selection of the "carbonyl" frequencies that have been obtained in Nujol mulls of the quinones are listed below and may be compared with the values of 1660 cm.$^{-1}$ (6.01 μ) for *p*-benzoquinone and 1676 cm.$^{-1}$ (5.97 μ) for anthraquinone, obtained previously by Flett.[2]

	cm.$^{-1}$	μ
p-Naphthoquinone	1664	6.01
Pyranthrone	1655	6.04
Mesonaphthadianthrone	1649	6.06
Helianthrone	1646	6.08
1,2;6,7-Dibenzpyrene-3,8-quinone	1645	6.08
Dibenzanthrone	1638	6.10
Diphenoquinone	1626	6.16

It can be seen that the "carbonyl" frequencies of the polynuclear quinones listed above vary considerably in value. Taking into account these results and those of the earlier workers[1,2] it appears that paraquinones in which the two quinone carbonyl groups occur in the same ring absorb in the range 1660 to 1680 cm.$^{-1}$, and that extended quinones, in which the carbonyl groups are in different rings, usually absorb in the range 1635 to 1655 cm.$^{-1}$. In confirmation of this latter point we have found that benzanthrone has its "carbonyl" band at 1644 cm.$^{-1}$, and anthrone has been shown previously to absorb at 1654 cm.$^{-1}$ [2]; both of these molecules have single carbonyl groups coupled in a similar fashion to polycyclic ring systems. A single exception to the above rule concerning the "carbonyl" frequencies of extended quinones is provided by diphenoquinone. However this result may be abnormal on account of the unusual structure and chemical properties of this molecule. In any case the above correlations must only be considered as provisional and as subject to refinement when the spectra of a more extensive series of molecules of this type become available. Other quinone type molecules for which we have observed low "carbonyl" frequencies are 3,3′- and 4,4′-dibenzanthronyl (1626 and 1630 cm.$^{-1}$, respectively). An insufficient number of orthoquinones seem to have been studied spectroscopically to enable correlation rules to be drawn up at present.

In picking out the "carbonyl" frequencies we have listed the strong absorption band for each compound which lies at the highest frequency in the region 1550 to 1750 cm.$^{-1}$. It is of interest to note however that in some cases other equally strong absorption bands occur in the infrared spectra in the region 1570 to 1600 cm.$^{-1}$.[3] As the skeletal vibrations of polycyclic ring systems often occur in this range[4] it seems probable that, as might be expected, several of these modes of vibration also involve considerable vibrational motion of the carbonyl linkages. This coupling with ring skeletal vibrations would explain at the same time the high intensity of these lower frequency absorption bands and the variable nature of the so-called carbonyl frequency itself. In all cases that we have so far investigated only very much weaker bands are found in the region 1550–1750 cm.$^{-1}$ for the corresponding hydrocarbons.

On further comparison of the spectra of the quinones and related hydrocarbons, differences were also found in the regions of the spectra which are not close to the "carbonyl" frequency. Thus in the spectra of the quinones strong absorption bands were found in region 1200–1350 cm.$^{-1}$ which are not present in comparable strength in the hydrocarbon spectra, and presumably also arise from the coupling of the $C{=}O$ vibration with those of the rest of the molecule. In addition the features in the spectra of the quinones and hydrocarbons between 900 and 700 cm.$^{-1}$ which can usually be attributed to the out-of-plane vibrations of the CH linkages attached to the aromatic skeleton[4] also showed considerable differences as would be expected from the changes in substitution pattern. Further spectroscopic work on these types of molecules is continuing.

We are very grateful to Professor A. R. Todd, F.R.S. and Dr. A. W. Johnson of the University Chemical Laboratory, Cambridge, and to Imperial Chemical Industries (Dyestuffs), Ltd., for samples of the substances studied.

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(1) M. L. Josien and N. Fuson, THIS JOURNAL, **73**, 478 (1951).

(2) M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948).

(3) A similar effect has been noted previously as being caused by the conjugation of a $C{=}O$ group to a phenyl ring (Randall, Fowler, Fuson and Dangl, "Infra-red Determination of Organic Structures," D. Van Nostrand and Co., New York, N. Y., 1949, p. 16).

(4) S. F. D. Orr and H. W. Thompson, *J. Chem. Soc.*, 218 (1950).

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Viscosity of Polytrifluorochloroethylene in o-Chlorobenzotrifluoride

BY H. TRACY HALL, EDWARD L. BRADY AND PAUL D. ZEMANY

Viscosity data for polytrifluorochloroethylene in a chlorofluorobutane solvent have been presented by H. S. Kaufman and M. S. Muthana.[1] We

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(1) Paper No. 26, Division of High Polymer Chemistry, American Chemical Society Meeting, September 5, 1950.

present here the results of measurements in the solvent *o*-chlorobenzotrifluoride at a temperature of 137.10°. The measurements were made with a Bingham-type viscometer in which flow times are measured as a function of driving pressure.

Experimental

The silicone oil constant temperature bath was electronically controlled at a temperature of 137.10 ± 0.02°. The viscometer was patterned after the one shown in ref. 2. with these modifications: (1) large stopcocks were placed in the arms approximately 10 cm. above A and M of the figure; and (2) a side arm containing a fritted glass disc and a 15-cc. bulb in which polymer and solvent were placed for dissolution was attached just above M. A weighed amount of polymer and 10 cc. (volume at 20°) of solvent were introduced into this bulb, a cap placed on the opening to the bulb and the stopcocks closed to keep solvent vapor from escaping. The solvent and polymer were left in the bulb until solution was complete. After solution, nitrogen gas under pressure was used to drive the solution through the fritted glass into the viscometer proper. Excess solution was withdrawn from the viscometer through a small stainless steel tube whose tip reached to point A in the left-hand arm. The solution was kept under an atmosphere of nitrogen at all times to prevent oxidation of the solvent.

A water manometer was used to determine driving pressure. Time of flow data as a function of driving pressure were obtained in the manner indicated in Appendix A of ref. 2. The viscometer was calibrated with water and sucrose solutions according to the methods outlined by Hall and Fuoss.[3] The volume of the dry bulb of the viscometer was 2.13 cc., the capillary radius was 0.015 cm., and the length of the capillary was approximately 10 cm.

Pressures were varied between 50 and 150 cm. of water in six approximately equal steps and the corresponding flow times recorded. In ref. 3 it is shown that the behavior of a solution in a Bingham-type viscometer can be expressed by the relationship

$$1/pt = A_0/\eta_\infty + (\kappa - \lambda)p \tag{1}$$

in which p is the driving pressure, t is the flow time, A_0 is a constant depending only on viscometer dimensions, η_∞ is the viscosity of the solution at zero driving pressure (infinite time), and κ and λ are functions of viscometer dimensions and the nature of the solution. For the viscometer used A_0 was 9.57×10^{-7} poise-cm.^{2}/g. sec.

The polytrifluorochloroethylene used was made by the Kellogg Corporation. The three molecular weight ranges used were designated Kel-F 240, lot no. 124; Kel-F 270, lot no. 126 and Kel-F 300, lot no. 162-L.

Results and Discussion

Plots of $1/pt$ *vs.* p were constructed and the viscosities at zero rate of shear for various concentrations of the polymer obtained from the intercepts. From the viscosities the reduced viscosities were calculated and plotted in the usual fashion as a function of concentration. The plots are shown in Fig. 1. The viscosity of the solvent *o*-chlorobenzotrifluoride at 137.10° is 0.3595 centipoise. The density is 1.20.

Molecular weights of 56,500, 76,000 and 100,000 are given for Kel-F 240, 270 and 300, respectively, by Kaufman and Muthana.[1] The relationship between intrinsic viscosity $[\eta]$ (obtained from the intercepts in Fig. 1) and the molecular weight M is expressed by the equation[4]

$$[\eta] = KM^\alpha \tag{2}$$

in which K is a constant and α is characteristic of the polymer and usually has a value between 0.3 and 1.2. Substituting the molecular weight values of Kaufman and Muthana into (2) and plotting $\log [\eta]$ *vs.* $\log M$ gives values of 1.71×10^{-4} and 0.77 for K and α, respectively, when the concentration is expressed as grams of polymer per 100 cc. of solvent. The value of α is somewhat of an indication of chain stiffness. The value obtained here is midway between that for a flexible chain polymer such as a polyester and that of a stiff chain polymer such as a cellulose derivative. This is consistent with what might be expected when a Hirschfelder model of the polymer is examined. The model shows that some restriction to rotation about C–C bonds should be expected.

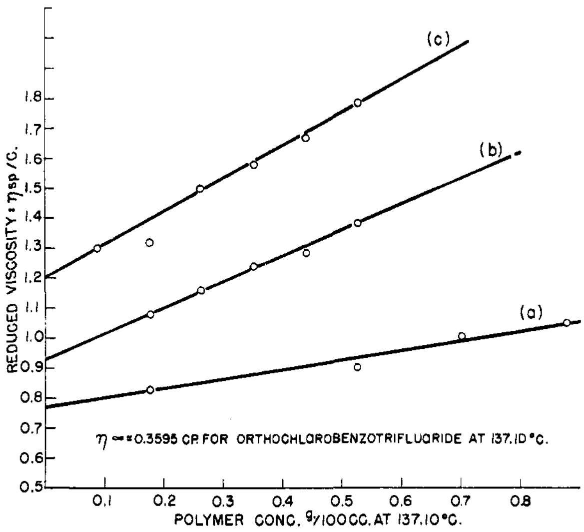

Fig. 1.—Reduced viscosity as a function of concentration for (a) Kel-F 240, (b) Kel-F 270 and (c) Kel-F 300 in orthochlorobenzotrifluoride at 137.10°.

It was not possible to evaluate shear constants[3] for this polymer because of a reduction in the precision resulting from difficulties introduced by the high temperature.

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[2] Eugene C. Bingham. "Fluidity and Plasticity." McGraw-Hill Book Co., Inc., New York, N. Y., Fig. 29, p. 76.

[3] H. T. Hall and R. M. Fuoss, THIS JOURNAL, 73, 265 (1951).

[4] H. Mark, "Die feste Körper," Verlag S. Hirzel, Leipzig, 1948, p. 103.

Perfluoro-*n*-propyl Disulfide and Perfluoro-*n*-propyl Trisulfide

BY MURRAY HAUPTSCHEIN AND ARISTID V. GROSSE

Molten sulfur reacted with 1-iodoheptafluoropropane under pressure at 250° to form perfluoro-*n*-propyl disulfide, $(CF_3CF_2CF_2)_2S_2$, and perfluoro *n*-propyl trisulfide, $(CF_3CF_2CF_2)_2S_3$. This represents the first satisfactory synthesis of these novel type perfluoroalkyl sulfur compounds. In this connection it should be mentioned that Bennett, Brandt, Emeléus and Haszeldine[1] reported very recently that thiocarbonyl fluoride (CSF_2) was a main product of the reaction of sulfur with iodotrifluoromethane, although at the reaction temperature of 205° there could be isolated a readily

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[1] F. W. Bennett, G. R. A. Brandt, H. J. Emeléus and R. N. Haszeldine, *Nature*, 166, 225 (1950).