yielded a 2,4-dinitrophenylhydrazone, m.p. 122.5–123°, undepressed by admixture with an authentic sample.[29] The 2,4-dinitrophenylhydrazone of isovaleraldehyde, m.p. 125.5–126°, strongly depressed the melting point of the above sample.

Neopentyl Iodide with Bromine.—Neopentyl iodide (92.0 mmoles) reacted with bromine (93.3 mmoles) in petroleum ether for 1.25 hours at −78° and 1.5 hours at 0° gave a very small amount (0.57 g., 4%) of an impure low boiling fraction, n^{22}_D 1.4448, b.p. 55–58° (120 mm.), micro b.p. 106°; reported[30] for *t*-amyl bromide, b.p. 108° (765 mm.), n^{20}_D 1.4421. There was not enough to refractionate.

Analysis was obtained on a similar material, probably *t*-amyl bromide, from an earlier run, b.p. 50.5–52° (115 mm.), n^{25}_D 1.4370.

Anal. Calcd. for $C_5H_{11}Br$: C, 39.75; H, 7.34. Found: C, 40.18; H, 7.45.

A higher boiling fraction on refractionation gave 2,3-dibromo-2-methylbutane, b.p. 74–75° (36 mm.), n^{22}_D 1.5020–1.5050, 7.04 g. (33% yield). Analysis was obtained on a similar material from an earlier run, micro b.p. 168–169°, n^{25}_D 1.5000.

Anal. Calcd. for $C_5H_{10}Br_2$: C, 26.11; H, 4.38. Found: C, 26.52; H, 4.32.

The structure was demonstrated by making the 2,4-dinitrophenylhydrazone of 3-methylbutanone-2 formed after first treating the dibromide with water in a sealed tube at 100° for six hours. No depression was obtained either with an authentic sample or with that obtained from the 2,3-dichloro-2 methylbutane (see above).

Reaction of *t*-Amyl Chloride with Chlorine.—*t*-Amyl chloride was chlorinated under the conditions described above for neopentyl iodide with the inclusion of an equivalent of iodine monochloride. Besides 44% of recovered starting material there was obtained 29% of 2,3-dichloro-2-methylbutane, b.p. 60–67° (104 mm.), n^{26}_D 1.4338–1.4415. The infrared spectrum of refractionated material, b.p. 66–67° (102 mm.), n^{26}_D 1.4405, was identical with that of authentic 2,3-dichloro-2-methylbutane (see above) and with the rearrangement product from the reaction of neopentyl iodide and chlorine.

t-Amyl chloride, chlorinated without iodine monochloride, was recovered almost unchanged.

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[29] A similar conversion of 2,3-dibromo-2-methylbutane to 3-methylbutanone-2 has been reported by F. C. Whitmore, W. L. Evers and H. S. Rothrock, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 408.

[30] N. A. Lange, "Lange's Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, Sixth Edition, 1946.

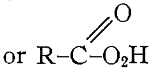
[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. III.[2] Structure of Aliphatic Peracids in Solution and in the Solid State. An Infrared, X-Ray Diffraction and Molecular Weight Study[3]

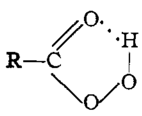
BY DANIEL SWERN, LEE P. WITNAUER, C. ROLAND EDDY AND WINFRED E. PARKER

RECEIVED APRIL 22, 1955

Infrared absorption spectra have been obtained on long-chain aliphatic peracids in solution (C_8–C_{16}) and in the solid state (C_{14}, C_{16}), and X-ray diffraction patterns have been obtained on the solid peracids (C_9–C_{16}). Infrared studies show that in solution the peracids exist exclusively as intramolecularly chelated monomers containing a five-membered ring (I). In the solid state the peracids, like the corresponding *n*-aliphatic acids and alcohols, occur as dimers (II) in which two of the monomer units are linked through intermolecular hydrogen bonds. The dimers, unlike those of the corresponding *n*-aliphatic acids and alcohols, dissociate completely to monomers when they are dissolved in a solvent. Molecular weight determinations in benzene support this last conclusion. In solution, peracids show a broad band of medium intensity at about 865 cm.$^{-1}$ (11.56μ), attributed to skeletal vibrations of the O–O bond. The peracids, unlike the even and odd numbered *n*-aliphatic acids, crystallize with the same end packing and angle of tilt, so that a plot of long spacings against number of carbon atoms yields a single straight line.

Although organic peracids have been known for about fifty years,[4] their structure (usually written as RCO_3H or  $R-\overset{/\!/O}{C}-O_2H$) has not been worked out unequivocally. Within the past five years several investigators have applied physical methods, particularly infrared (which has proved to be the most fruitful), to the solution of this problem.[5–11] These workers studied only the lowest aliphatic peracids[7–11] (performic, peracetic, perpropionic and perbutyric acids) and perbenzoic acid.[5,6] The short-chain peracids are corrosive liquids and they are difficult to obtain and keep in a pure state completely free of water, hydrogen peroxide and/or the corresponding carboxylic acid. They are quite unstable (performic acid is explosive[7]) and readily attack the cells used in determining their infrared spectra. Perbenzoic acid although it is a solid which can be readily purified, is a more complicated compound to study because of the absorption characteristics of the phenyl group.

In spite of these difficulties certain conclusions have been reached. Giguère and Olmos[7] reported that performic and peracetic acids exist exclusively as hydrogen bonded, intramolecularly chelated monomeric substances (I), both in the liquid and vapor states. These investigators described an approximate configuration of the percarboxyl group and also gave interatomic distances. The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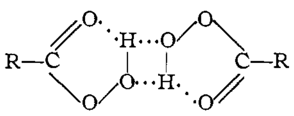
II

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[1] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Part II, THIS JOURNAL, **77**, 4037 (1955).

[3] Presented at the Fall Meeting of the American Chemical Society, Minneapolis, Minn., September 11–16, 1955.

[4] D. Swern, *Chem. Revs.*, **45**, 1 (1949).

[5] E. Briner and P. de Chastonay, *Compt. rend.*, **238**, 32 (1954).

[6] W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

[7] P. A. Giguère and A. Weingartshofer Olmos, *Can. J. Chem.*, **30**, 821 (1952).

[8] D. G. Knorre and N. M. Emanuel, *Zhur. Fiz. Khim.*, **26**, 425 (1952).

[9] Z. K. Maizus, V. M. Cherednichenko and N. M. Emanuel, *Doklady Akad. Nauk S.S.S.R.*, **70**, 855 (1950).

[10] G. J. Minkoff, *Proc. Roy. Soc. (London)*, **A224**, 176 (1954).

[11] B. S. Neporent, T. E. Pavlovskaya, N. M. Emanuel and N. G. Yaroslavskiĭ, *Doklady Akad. Nauk S.S.S.R.*, **70**, 1025 (1950).

spectroscopic results did not permit deciding between a planar or slightly puckered five-membered chelate ring. Davison,[6] on the basis of an infrared study and the melting point, concluded that perbenzoic acid, m.p. 41°, is normally monomeric in solution and that chelation is dimensionally possible if the skew configuration of the peroxide bond is somewhat nearer to a *cis* configuration. Minkoff[10] has stated that from his infrared studies alone it cannot be decided whether the hydrogen bonding is inter- or intramolecular, but Davison[6] and Giguère and Olmos[7] give considerable evidence that chelation is more important than dimerization.

In our previous paper,[2] we described the preparation of crystalline, relatively stable aliphatic peracids, containing up to 18 carbon atoms. Most of these (C_8–C_{16}) were obtained in extremely high purity, completely free of the contaminants usually found in the lower molecular weight peracids studied by previous investigators. The availability of pure solid peracids prompted us to conduct an infrared examination of them in solution and in the solid state using a high-resolution infrared spectrophotometer. X-Ray diffraction powder patterns and molecular weights in benzene also were obtained.

Experimental

Starting Materials.—The preparation of percaprylic, perpelargonic, percapric, perhendecanoic, perlauric, pertridecanoic, permyristic and perpalmitic acids already has been described.[2]

Infrared Absorption Spectra.—These were obtained with a Beckman IR-3 spectrophotometer using sodium chloride prisms. The peracid solutions decomposed in the amalgamated cells producing a green color and a sharp band at 2335 cm.$^{-1}$ first noticeable after about 15 minutes. On the other hand, the solutions showed no change in spectrum on standing several hours in glass flasks at room temperature. The spectra, therefore, were run in sections each requiring no more than 12 minutes, the cells being rinsed and filled with fresh solution for each section. The mulls appeared to be stable. For the mulled samples, a demountable cell with a moat-type channel in one window was used,[12] with a spacer approximately 0.03 mm. thick. The mineral oil absorption was partially compensated by a tape-recorded blank using pure mineral oil in the same cell with a spacer approximately 0.02 mm. thick. This method cannot compensate exactly for the three strongest absorption bands of the mineral oil because of the non-quantitative nature of a mull.

X-Ray Diffraction Patterns.—Powder patterns were recorded with a powder camera, 14 cm. in diameter, using CrKα radiation. Specimens were prepared by pressing a finely ground sample on a glass slide and cutting from it a narrow section 0.3 mm. thick.

Molecular Weights.—These were determined cryoscopically in benzene by the usual procedure.

Results and Discussion

Infrared Spectra.—In solution, the infrared spectra of all the aliphatic peracids examined are basically the same, showing only minor variations with chain length. The only two peracids examined in the solid state (C_{14} and C_{16}) show no significant differences in spectra for wave numbers greater than 1300 cm.$^{-1}$. In the 700–1300 cm.$^{-1}$ region, these two solids show many bands not found in the solution spectra. These bands appear to form wave-number progressions that are distinctly different for the two different chain lengths. Since most of the work was done on perpalmitic acid, this is the only peracid whose spectra are reported (Figs. 1 and 2). For comparison, the spectra of palmitic acid and cetyl alcohol also are given.

As Fig. 1 shows, the hydroxyl stretching vibration of the peracids (curves A and B) is found at 3280 cm.$^{-1}$ (3.05 μ) in carbon tetrachloride solution. The position of this band shows no change with concentration and its absorptivity shows only slight change. For all the peracids studied (except percaprylic acid) the average of all molar absorptivities at all concentrations is $\epsilon = 51.6$ liters per mole per centimeter. The maximum variation from this at any one concentration was only 3%, although each compound was examined at concentrations from 0.006 to at least 0.3 mole per liter. The position of this band compared to that of the unassociated fatty acid at 3530 cm.$^{-1}$ (2.83 μ) and of the unassociated alcohol at 3635 cm.$^{-1}$ (2.75 μ) (curve F), shows that the peracids are hydrogen bonded. The insensitivity of the band to dilution indicates that in solution the hydrogen bonding is intramolecular.

At as low a concentration as 0.006 *M*, peracids show no evidence of an unassociated hydroxyl band; only the band of associated hydroxyl can be seen. On the other hand, palmitic acid at 0.006 *M* shows not only the strong, broad dimer band but also a very sharp, unassociated-hydroxyl band at 3530 cm.$^{-1}$ ($\epsilon = 22.2$). Davies[13,14] states that carboxylic acids begin to show a weak but definite band due to unassociated hydroxyl at 0.01 to 0.02 *M*. Cetyl alcohol shows both associated and unassociated ($\epsilon = 27.6$) bands at as high a concentration as 0.33 *M* (curve F). Since an equilibrium exists between monomeric and dimeric alcohols and between monomeric and dimeric carboxylic acids in solution, with the extent of dimerization varying with the concentration, it must be concluded that the peracids exist in solution solely as intramolecularly hydrogen-bonded monomers. The structure proposed by Giguère and Olmos[7] (I) for performic and peracetic acids is a reasonable one for the entire homologous series of aliphatic peracids.

In the solid state, however, the hydroxyl band of the peracids (Fig. 2, curve A) is shifted to even lower frequencies (3200 cm.$^{-1}$, 3.13 μ) and is broader than in solution. This broadening and larger shift of frequency suggests that in the solid state the peracids, like the carboxylic acids, are intermolecularly hydrogen bonded. (Intermolecular bonding in the solid state is discussed in more detail later.) In comparison, cetyl alcohol in the solid state (curve C) has its hydroxyl band at about 3250 cm.$^{-1}$ (3.1 μ), and palmitic acid (curve B) has the usual broad band centered roughly around 2900 cm.$^{-1}$ (3.4 μ). Thus, the hydroxyl band of the solid peracids is between that of alcohols and carboxylic acids, but is much nearer to that of the alcohols. The solid peracids, therefore, are slightly more strongly intermolecularly hydrogen bonded than are the solid alcohols but not nearly so strongly as the solid acids.

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[12] J. S. Ard, *Anal. Chem.*, **23**, 680 (1951), and private communication.

[13] M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 755 (1938).

[14] M. M. Davies, *ibid.*, **8**, 577 (1940).

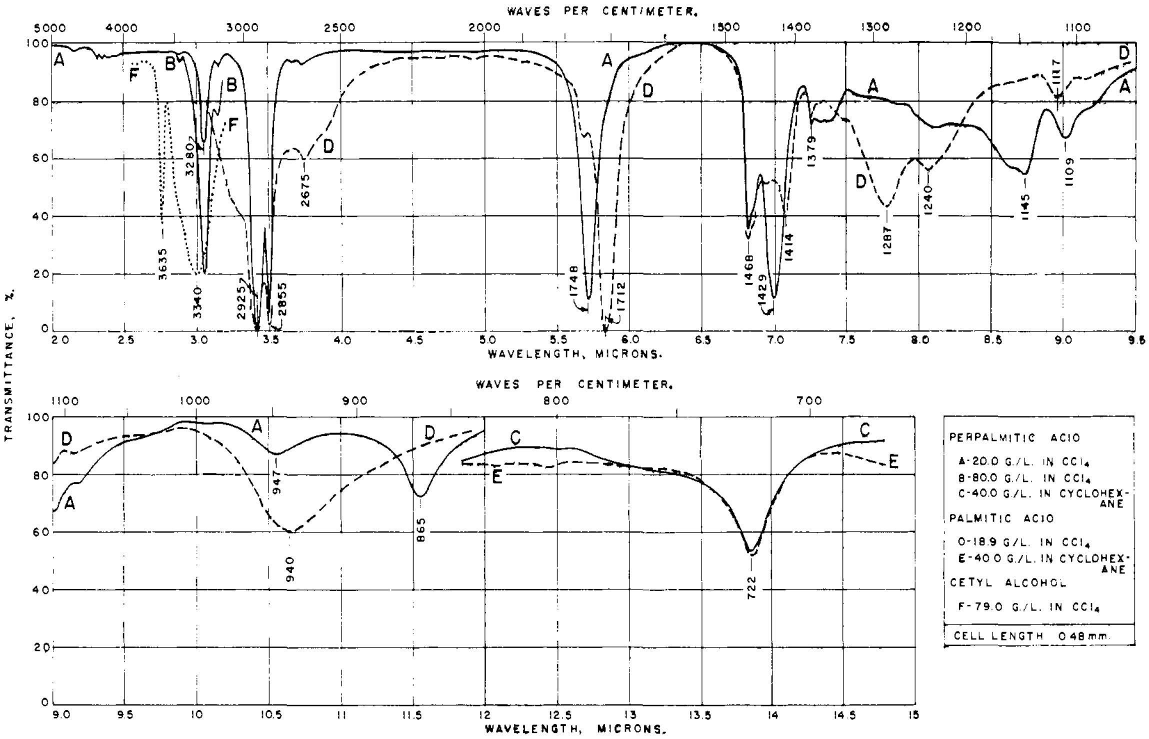

Fig. 1.—Infrared spectra of perpalmitic acid (A, B, C), palmitic acid (D, E), and cetyl alcohol (F) in solution.

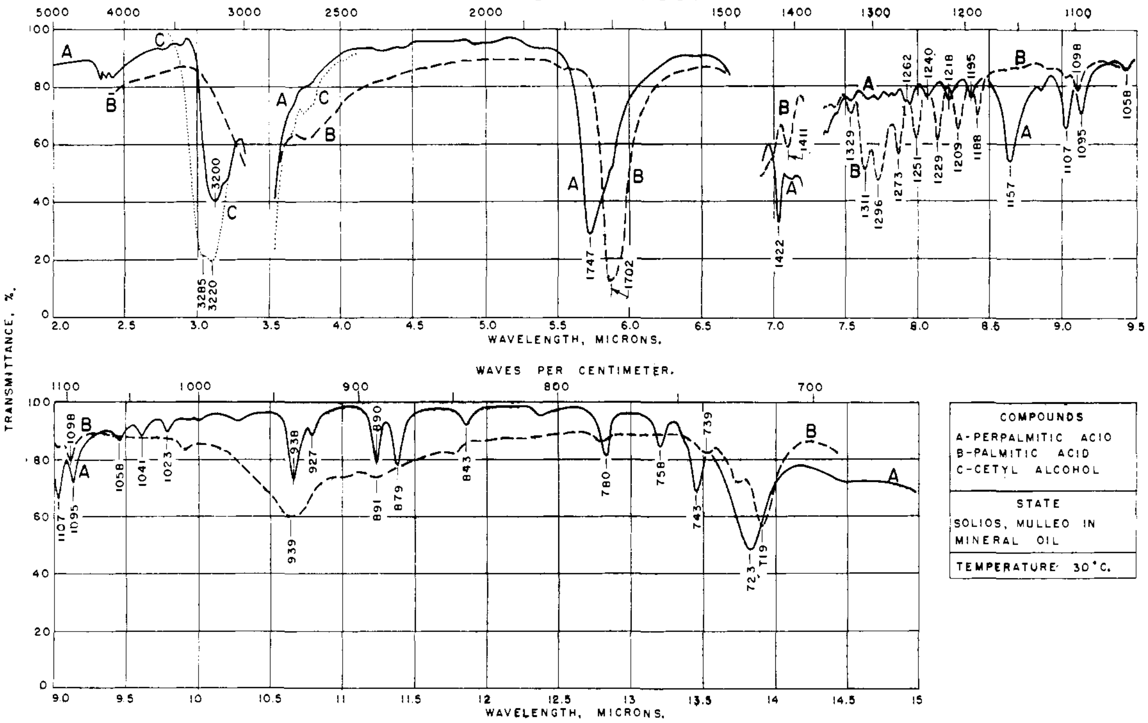

Fig. 2.—Infrared spectra of perpalmitic acid (A), palmitic acid (B), and cetyl alcohol (C) in the solid state.

Peracids have a strong, single carbonyl absorption band at 1747–1748 cm.$^{-1}$ (5.72 μ) both in solution (Fig. 1, curve A) and in the solid state (Fig. 2, curve A), although in the latter case the band is slightly less sharp. Carboxylic acids in solution (Fig. 1, curve D) have a strong absorption band due to the carbonyl group at about 1708–1712 cm.$^{-1}$ (5.85–5.84 μ)[15,16] which shifts to slightly lower frequencies[16] (1698–1705 cm.$^{-1}$, 5.89–5.87 μ) in the solid state (Fig. 2, curve B). In solution (curve D),

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[15] O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **22**, 1498 (1950).

[16] R. G. Sinclair, A. F. McKay and R. N. Jones, THIS JOURNAL, **74**, 2570 (1952).

carboxylic acids also show a weak carbonyl band at about 1760 cm.$^{-1}$ (5.68 μ), attributed to the monomeric carbonyl group, which is not present in the solid state spectra.[13,16] The peracids, however, show no evidence of unbonded carbonyl group under any conditions which we have studied, which is in accord with the conclusion that they are completely chelated.

The shift of the carbonyl frequency parallels the shift of the hydroxyl frequency. If one assumes that the frequency of an unbonded carbonyl lies near 1760 cm.$^{-1}$ (5.68 μ) in peracids (as it does in carboxylic acids[13,16]), then the shift of the peracids to 1747–1748 cm.$^{-1}$ (5.72 μ) on forming the chelate is less than the shift to 1705–1725 cm.$^{-1}$ (5.87–5.80 μ) in the carboxylic acid dimers.[17] As with the hydroxyl band, the carbonyl frequency thus also suggests that the hydrogen bonding is less strong in the peracid chelate than in the carboxylic acid dimer. The failure of peracids to produce an unassociated carbonyl (or hydroxyl) absorption band on high dilution, however, is a consequence of a favorable steric situation.

Like the fatty acids,[18] the peracids show the methylenic deformation vibration at 1468 cm.$^{-1}$ (6.81 μ) and the symmetric methyl deformation at 1379 cm.$^{-1}$ (7.25 μ) the latter increasing in strength as chain length decreases. The asymmetric methyl deformation appears as a weak, resolved peak at 1460 cm.$^{-1}$ (6.85 μ) for C_{10} and lower, increasing in strength as chain length decreases. The 1429 cm.$^{-1}$ (7.00 μ) band is present in all the peracids examined, with molar absorptivity in the range 244 to 267. A band in this vicinity was discussed by Minkoff.[10] Although it is found in a wide variety of hydroperoxides and peroxides, it does not seem justified to assign it to any particular vibration at present. In the 1100–1150 cm.$^{-1}$ (9.09–8.70 μ) region, the peracids have two moderately strong bands, varying in location and contour with chain length. These may possibly be related to the bands found near 1235 (8.10 μ) and 1285 cm.$^{-1}$ (7.78 μ) in the fatty acid series.[19]

The strong broad absorption at about 940 cm.$^{-1}$ (10.64 μ) (Fig. 1, curve D) occurs in the solution spectra of many carboxylic acids, and may arise from vibrations of the O–H group in and out of the plane (deformation mode) of the carboxyl group.[13,20] The peracids in solution (Fig. 1, curve A) show much weaker absorption in this region (947 cm.$^{-1}$, 10.56 μ). In the solid state, however, this band is sharpened considerably and, in the peracids, is shifted to lower frequency (Fig. 2, curve A) whereas that of the carboxylic acids (Fig. 2, curve B) is essentially unchanged. As Bellamy points out,[21] the band in this region would be expected to show marked changes associated with changes of state which may alter the degree of hydrogen bonding. This supports the conclusion suggested earlier from other spectral evidence that peracids are both intermolecularly and intramolecularly hydrogen bonded in the solid state.

Although skeletal vibrations of the O–O group in peroxides, hydroperoxides and peracids[6,10,22–24] have a wide frequency range, it is fairly clear that aliphatic materials of these types absorb in the 870 cm.$^{-1}$ (11.49 μ) region. In solution (Fig. 1, curve A) peracids show a broad band of medium intensity at about 865 cm.$^{-1}$ (11.56 μ), absent in the corresponding carboxylic acids. In the solid state (Fig. 2, curve A) this band is difficult to assign.

The band shown at about 720 cm.$^{-1}$ (13.9 μ) by both the peracids and the corresponding carboxylic acids in solution or in the solid state is observed in a large number of long chain compounds containing a continuous chain of four or more carbon atoms.[25] It has been ascribed to a $-CH_2-$ rocking mode.[26,27] By means of infrared spectra the peracids can be distinguished most conveniently from the corresponding carboxylic acids by the bands near 865, 1430 and 3280 cm.$^{-1}$.

X-Ray Diffraction Studies.—The tentative conclusion from infrared evidence that aliphatic peracids in the solid state exist as intermolecularly hydrogen bonded dimers was confirmed fully by X-ray diffraction studies. Table I shows the long-spacings of the C_9–C_{16} aliphatic peracids. (The C_{18}-peracid, perstearic acid, could not be purified completely. The melting points of the C_6- and C_8-peracids are too low to be handled in our equipment.)

Table I

Long Spacings of Aliphatic Peracids

Peracid	Long spacing, Å.
Perpelargonic (C_9)	22.30
Percapric (C_{10})	24.55
Perhendecanoic (C_{11})	26.82
Perlauric (C_{12})	28.84
Pertridecanoic (C_{13})	31.06
Permyristic (C_{14})	33.12
Perpalmitic (C_{16})	37.19

The long-spacing increases regularly as the hydrocarbon chain increases. The average increase for each additional carbon atom is approximately 2.11 Å., which is considerably greater than the expected projected distance, 1.27 Å., of one C–C bond. It appears that the long spacing measured as the diffraction photographs are the projections of double the molecular length on [d001]. Thus the peracid molecules, like the *n*-aliphatic acids and alcohols, must crystallize in bimolecular layers. The increase in long spacing for each additional carbon atom is 2.11/2 = 1.06 Å., which is lower than the anticipated value of 1.27 Å. Peracid dimers, therefore, are tilted with respect to the 001 plane.

When the long spacings of the C_9–C_{16} peracids are plotted against the number of carbon atoms

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(17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 143.

(18) Reference 17, pp. 19–20.

(19) Reference 17, p. 147.

(20) D. Hadži and N. Sheppard, *Proc. Roy. Soc.* (*London*), **A216**, 247 (1953).

(21) Reference 17, p. 148.

(22) Reference 17, p. 105.

(23) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 282 (1951).

(24) H. R. Williams and H. S. Mosher, *ibid.*, **27**, 517 (1955).

(25) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

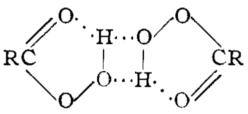
(26) Reference 17, p. 26.

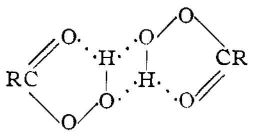
(27) N. Sheppard and G. B. B. M. Sutherland, *Nature*, **159**, 739 (1947).

(Fig. 3), a straight line is obtained. The long spacings of the even and odd numbered peracids do not fall on separate lines, as has been observed for the corresponding *n*-aliphatic acids, thus suggesting that the packing of the ends of the even and odd peracids are the same. Therefore, it follows that the melting points of the even and odd numbered peracids should show no discontinuity. This is in accord with the experimental facts.[2]

As Fig. 3 shows, a plot of the long spacings of the C-form of the *n*-aliphatic acids containing an even number of carbon atoms against number of carbon atoms yields a line parallel to that obtained with the peracids. This suggests similar angles of tilt. The long-spacings of the peracids are approximately 1.3 Å. larger than those of the corresponding acids.

It was hoped that a comparison of dimer lengths (calculated from known bond distances and angles obtained from a few possible peracid models) with the measured long spacings would lead to a direct establishment of their structure. This was not possible because the molecules are tilted, and the packing at the ends and the puckering (if any) of the five-membered chelate ring are not known. The X-ray diffraction data and the infrared studies in this Laboratory and elsewhere[7] suggest the following possible structures for the peracids in the solid state





These structures are schematic and are not intended to suggest that the percarboxyl groups are necessarily coplanar. No information is yet available on the extent of skewing or puckering, if any. Examination of molecular models indicates that both structures are possible.

When solid peracids are dissolved in a solvent, the four-membered ring should cleave easily because the hydrogen bonding capacity of each hydrogen atom is divided between two oxygen atoms. The intramolecular bond is by far the strongest because of the configuration of the percarboxyl group.

Molecular Weight Studies.—If peracids exist exclusively as intramolecularly hydrogen bonded monomers in solution, their molecular weight should remain constant regardless of concentration (provided that one remains within the concentration range of "ideal" solutions). Molecular weight studies were limited to a comparison of the molecular weights of lauric and perlauric acids. At 0.03 *M* in benzene, lauric acid (calculated molecular weight, 200) had a molecular weight of 337, indicating about 70% dimer and 30% monomer; at 0.07 *M* the molecular weight was 378, indicating about 90% dimer and 10% monomer. Perlauric acid (calculated molecular weight, 216), on the other hand, over the concentration range 0.02–0.05 *M*, showed essentially a constant molecular weight of 208 ± 3.5%.

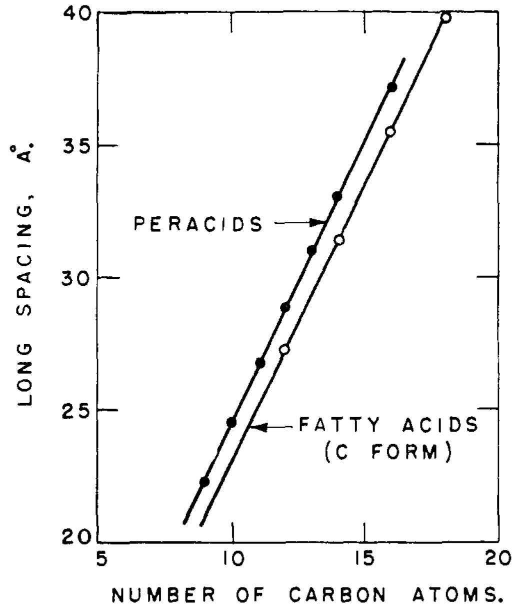


Fig. 3.—Long spacings of C_9-C_{16} aliphatic peracids.

Miscellaneous.—A consequence of the proposed chelated structure of peracids is that they should be considerably weaker acids than the corresponding carboxylic acids. Studies with short-chain peracids in essentially aqueous systems[28,29] have shown this to be the case. The *pK* value ("*p*H" of half neutralization) of perlauric acid in alcohol solution is about 10.8; that of lauric acid is about 7.8. The end-point in the titration of the peracid is not nearly so sharp as that of the carboxylic acid and occurs at a "*p*H" of 12 which is 2 "*p*H" units higher. The difference between the acid strength of the peracid and the carboxylic acid in the non-aqueous system is about the same as that in aqueous systems.

Acknowledgment.—The authors thank Mary-Anne Barnes for assistance in obtaining and processing the infrared spectra.

PHILADELPHIA, PENNA.

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(28) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

(29) R. Wolf, *Bull. soc. chim. France*, 644 (1954).