[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE, AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Determination of Double-bond Character in Cyclic Systems. II. The 9,10-Bond of Phenanthrene

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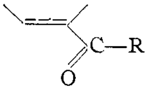
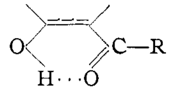
On the basis of evidence derived both from chemical reactions and infrared spectra the highly olefinic nature of the 9,10-bond in phenanthrene is confirmed. The intramolecular hydrogen bonds in 9,10-disubstituted phenanthrenes are shown to be the strongest such bonds yet encountered in simple aromatic compounds. A linear relationship is demonstrated between the degree of double-bond character of the ring bonds in various aromatic hydrocarbons and the "$\Delta\nu$(C=O) values" for these bonds as determined from the infrared spectra of appropriate monosubstituted and chelated disubstituted derivatives of these hydrocarbons. The effect upon hydroxyl and carbonyl vibrational frequencies of conjugation with aromatic rings is summarized. Some interesting chemical properties are postulated for the as yet unknown 10-hydroxy-9-phenanthrenecarboxylic acid, and the ease of decarbonylation of 10-hydroxy-9-phenanthrenecarboxaldehyde is noted. A variation of the N-methylformanilide synthesis of aromatic aldehydes is presented.

Introduction

In the first paper[2] of this series, it was found that shifts in the carbonyl vibrational frequency, caused by conjugated chelation of an aldehyde, ketone or ester substituent with adjacent hydroxyl groups, depended upon the double-bond character of the bond between the carbon atoms holding the substituents. The C=O absorption frequencies were observed in the infrared spectra of the monosubstituted carbonyl-containing compounds (I) and in the spectra of the chelated *o*-hydroxyl derivatives (II) in the benzene and naphthalene series. The decrease in the C=O frequency (in cm.$^{-1}$) in the chelated form (II) with respect to that in the non-chelated form (I) was defined as $\Delta\nu$(C=O)[3] for the chelated compound. The $\Delta\nu$(C=O) values for the 1,2-(or 2,1-) and 3,2-disubstituted naphthalenes were almost an equal amount greater, and less, respectively, than the $\Delta\nu$(C=O) values for the analogous benzene derivatives, demonstrating a correlation between the $\Delta\nu$(C=O) values and the double-bond character of the nuclear bond in the chelate ring (II). This paper presents the results of a similar spectral investigation of the 9,10-bond in phenanthrene, and develops a quantitative relationship between the $\Delta\nu$(C=O) values and double-bond character.



I



II

R = H, CH_3, OCH_3

In the case of phenanthrene, Pauling,[4] by neglecting ionic structures, has assigned 80% double-bond character to the 9,10-bond and a considerable amount of chemical evidence indicates that this bond is even more olefinic than the 1,2-bond of naphthalene. Thus, phenanthrene adds bromine and is oxidized and reduced at the 9,10-positions under conditions to which the 1,2-bond of naphthalene is either inert or much less reactive.[5] Furthermore, the 9,10-bond of phenanthrene, but not the 1,2-bond of naphthalene, appears able to function as the "allyl double bond" in rearrangements of the Claisen type.[6] In addition to the spectroscopic results for the 9,10-bond in phenanthrene, some significant new chemical evidence bearing on the nature of this bond will be described.

Discussion

Chemical Results.—Of the phenanthrene compounds of types I and II required for this research only the methyl ester (III) of 10-hydroxy-9-phenanthrenecarboxylic acid has not been described previously. Our original attempts to prepare this ester were directed toward the corresponding hydroxy acid, which, however, we were unable to prepare either by high-pressure carbonation of 9-phenanthrol (IV) or by oxidation of 10-hydroxy-9-phenanthrenecarboxaldehyde (V). Finally, we obtained the desired hydroxy ester (III) by demethylating (66% crude yield) the corresponding methoxy ester (VI), which was prepared (94% crude yield) from the methoxy acid (VII) and diazomethane. Saponification of III by heating with dilute aqueous alkali and then acidifying at low temperature gave 9-phenanthrol (IV) in 50% yield as the only product identified. This very interesting result probably is one of the best pieces of chemical evidence substantiating the highly olefinic nature of the 9,10-bond, since it requires that 10-hydroxy-9-phenanthrenecarboxylic acid be an unusually "intense" vinylog of carbonic acid; this is possible only if the 9,10-bond is highly olefinic.[7] This consideration also seems adequate to explain the behavior of 10-hydroxy-9-phenanthrenecarboxaldehyde (V) on oxidation. Thus, Pearl's silver oxide oxidation procedure,[8] when applied at room temperature to this aldehyde, gave either unchanged V or, if the reaction time was pro-

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[2] I. M. Hunsberger, THIS JOURNAL, **72**, 5626 (1950).

[3] This term is considered more descriptive than "ΔC=O," which was used in the previous paper (ref. 2).

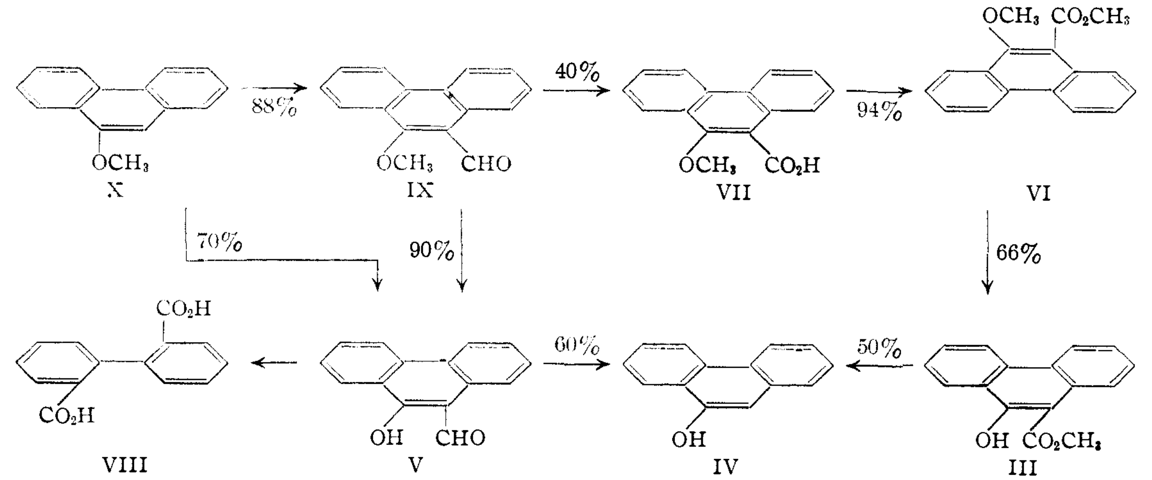
[4] L. Pauling, "The Nature of the Chemical Bond," Second Edition, Cornell University Press, Ithaca, N. Y., 1940, p. 142.

[5] For a review of this evidence, see L. F. Fieser in Gilman's "Organic Chemistry—An Advanced Treatise," Vol. I, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 160–162.

[6] D. S. Tarbell and V. P. Wystrach, THIS JOURNAL, **65**, 2149 (1943).

[7] It may be important to note that, although both 2-hydroxy-1-naphthoic acid and 1-hydroxy-2-naphthoic acid are equally "intense" vinylogs of carbonic acid, the former is much more readily decarboxylated than the latter; for example, the former is reported [R. Schmitt and E. Burkard, *Ber.*, **20**, 2699 (1887)] to decarboxylate on recrystallization from ethanol above 30–40°. It is interesting that with respect to the carboxyl group 2-hydroxy-1-naphthoic acid is more strictly comparable to 10-hydroxy-9-phenanthrenecarboxylic acid than is 1-hydroxy-2-naphthoic acid.

[8] I. A. Pearl, *J. Org. Chem.*, **12**, 85 (1947).



longed, diphenic acid (VIII).[9] It also may be significant to observe that the standard procedure for demethylation, *i.e.*, refluxing in acetic acid with 48% hydrobromic acid, when applied to 10-methoxy-9-phenanthrenecarboxaldehyde (IX), produced a very low yield of **9-phenanthrol** (IV) as the only product we were able to identify. The hydroxyaldehyde (V) apparently resembles the vinylogous formic acid, because the former was decarbonylated smoothly when refluxed with acetic and hydrobromic acids to produce 9-phenanthrol (IV) in 60% yield (recrystallized).

Mosettig and Burger[10] prepared the hydroxy aldehyde (V) from 9-phenanthrol by the Gattermann reaction. On subjecting 9-methoxyphenanthrene (X) to the conditions used in preparing 2-methoxy-1-phenanthrenecarboxaldehyde[11] *via* the N-methylformanilide synthesis, we obtained an 88% crude yield of methoxy aldehyde (IX). However, when this reaction was allowed to proceed for three hours in an oven at 70° and the crude product, which always melted somewhere in the range 80–92° (uncor.), was reheated for five hours at 75° with the same quantities of reagents as were used in its preparation, yields of recrystallized hydroxy aldehyde (V), m.p. 134–135.5° (uncor.), as high as 70% (based on X) regularly were obtained. The identity of V was confirmed by preparation of the known anil and by the previously mentioned oxidation to *unsubstituted* diphenic acid (VIII). We were unable to find conditions suitable for preparing V from 9-methoxyphenanthrene without isolating and retreating the above product (m.p. in the range 80–92°) of undetermined composition. When the preformed methoxyaldehyde (IX) was heated five hours at 75° under the conditions used in the N-methylformanilide synthesis, a 90% yield of recrystallized hydroxy aldehyde (V), m.p. 135–136° (uncor.), was obtained. However, when the N-methylformanilide was omitted from the reaction, only an intractable blackish-purple solid was obtained. Hence, it is likely that the N-methylformanilide acted only as a suitable solvent for the reaction. Apparently no previous cases of demethylation accompanying the N-methylformanilide synthesis have been reported,[12] and the ease of this demethylation very likely can be ascribed to the highly olefinic nature of the 9,10-bond of phenanthrene.

Infrared Results.—The infrared absorption spectra of the solid phenanthrene derivatives are given in Fig. 1 for the Nujol mulls; they are presented primarily for their analytical significance. In Fig. 2 are the spectra, in the 3 and 6μ regions, of the same compounds in 0.02 molal solutions in carbon tetrachloride. The frequencies of the carbonyl absorption bands in the solids and also in the solutions are summarized in Table I along with the $\Delta\nu$(C=O) values determined from the data for the solutions.

TABLE I

FREQUENCIES OF THE CARBONYL ABSORPTION BANDS AND $\Delta\nu$(C=O) VALUES FOR THE PHENANTHRENE DERIVATIVES

Compound	Frequency, cm.$^{-1}$ In Nujol	In 0.02 *M* CCl$_4$[a]	$\Delta\nu$ (C=O)
9-Phenanthrenecarboxaldehyde	1687	1698	..
Methyl 9-phenanthryl ketone	1667	1685	..
Methyl 9-phenanthrenecarboxylate	1712	1724	..
10-Hydroxy-9-phenanthrenecarboxaldehyde (V)	1629	1637	61
Methyl 10-hydroxy-9-phenanthryl ketone	1611 medium 1596 shoulder 1590 strong	1610	75
Methyl 10-hydroxy-9-phenanthrenecarboxylate (III)	1637	1649	75

[a] Observed at a cell thickness of 0.32 mm. except for the last entry, methyl 10-hydroxy-9-phenanthrenecarboxylate (III), which was at 0.16 mm.

The $\Delta\nu$(C=O) values for the phenanthrene compounds are about 75 cm.$^{-1}$ compared to values near 55 cm.$^{-1}$ for the corresponding 1,2-(or 2,1-) disubstituted naphthalenes. Hence, it seems safe to conclude that intramolecular hydrogen bonding between ortho hydroxyl and carbonyl-containing substituents is stronger for the 9,10-phenanthrene derivatives than for the 1,2-(or 2,1-) naphthalenes.

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[9] Pearl's oxidation procedure gave a 45.5% yield of 2-hydroxy-1-naphthoic acid from 2-hydroxy-1-naphthaldehyde (ref. 2).

[10] E. Mosettig and A. Burger, THIS JOURNAL, **55**, 2981 (1933).

[11] J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton and G. P. Turner, *ibid.*, **63**, 1334 (1941).

[12] K. J. Karrman [*Svensk Kem. Tidsk.*, **58**, 293 (1946)] briefly refers to a "sirup giving an aldehyde reaction" which he prepared from 9-retenol and N-methylformanilide.

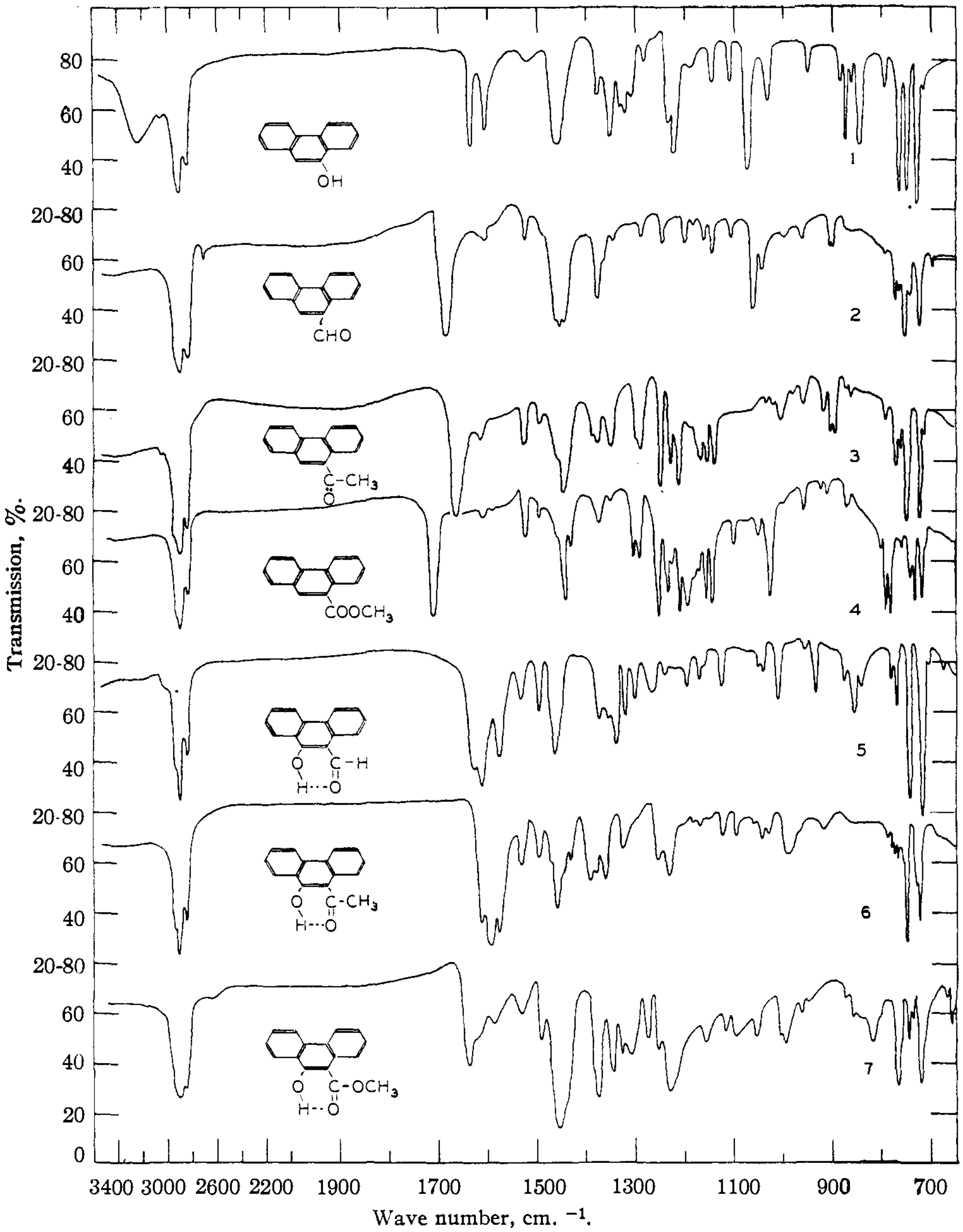

Fig. 1.—Infrared absorption spectra of the solid phenanthrene compounds as mulls in Nujol.

In view of the earlier observation[2] that the strength of such chelation was related to the double-bond character of the aromatic ring bond, a larger amount of double-bond character must be assigned to the 9,10-phenanthrene bond than to the 1,2-naphthalene bond. This conclusion agrees with the vinylogy principle,[13] which should operate with greater intensity in a 9,10-disubstituted phenanthrene than in analogous derivatives of any other common aromatic ring system.

In the previous work,[2] an attempt to assign $\Delta\nu$(OH) values was relatively unsuccessful because of the difficulty in locating accurately the greatly shifted and broadened OH bands in the strongly chelated disubstituted compounds. However, in most of the disubstituted naphthalenes and benzenes, all but the most strongly chelated compounds showed at least a hint of an OH band in the vicinity of the C–H vibrational band sat about 3000 cm.$^{-1}$. On the other hand, as may be seen in Fig. 2, there is no trace of an OH band in any of the disubstituted phenanthrenes. This is additional evidence for the greater strength of chelation in the phenanthrene compounds.

Another effect of interest is related to conjugation of the hydroxyl or carbonyl group with the aromatic ring system in the *monosubstituted* derivatives. In the previous work[2] it was found that the OH and C═O vibrational frequencies were slightly lower in the naphthalene derivatives than in the benzene derivatives. Now the 9-monosubstituted phenanthrenes have been found to exhibit somewhat lower OH and C═O vibrational frequencies than the monosubstituted naphthalenes, but the difference between the naphthalene and phenan-

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[13] R. C. Fuson, *Chem. Revs.*, **16**, 1 (1935).

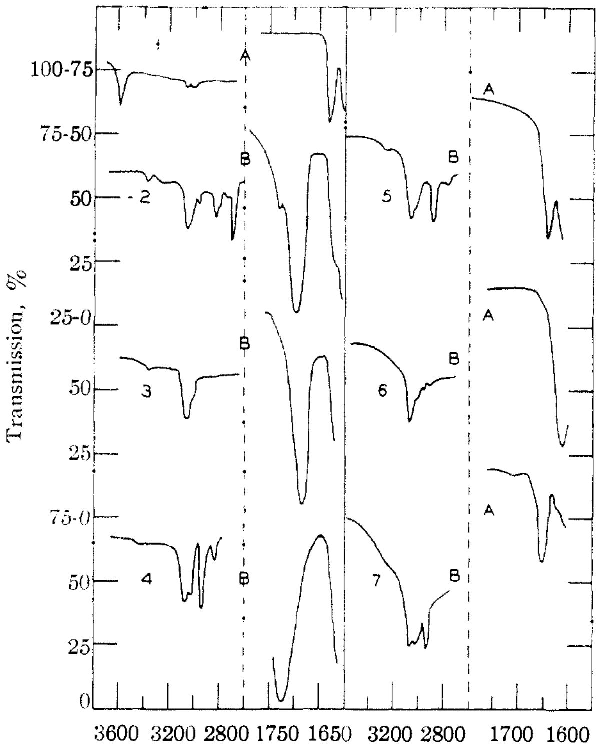
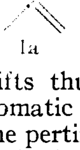
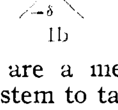


Fig. 2.—Infrared absorption spectra, in the 3 and 6μ regions, of the phenanthrene compounds in 0.02 molal solution in carbon tetrachloride: 1, 9-phenanthrol; 2, 9-phenanthrenecarboxaldehyde; 3, methyl 9-phenanthryl ketone; 4, methyl 9-phenanthrenecarboxylate; 5, 10-hydroxy-9-phenanthrenecarboxaldehyde; 6, methyl 10-hydroxy-9-phenanthryl ketone; 7, methyl 10-hydroxy-9-phenanthrene carboxylate. A, 0.32 mm. cell; B, 1.5 mm. cell.

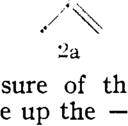
threne compounds is even less than that between the naphthalene and benzene compounds. These vibrational frequencies depend presumably upon conjugation of the substituent with the aromatic system to give canonical forms such as 1b and 2b. In 1b, the OH stretching frequency is decreased because the oxygen is more electropositive than in 1a; while in 2b, the carbonyl bond acquires single-bond character, decreasing the vibrational frequency from that of the double bond in 2a. The



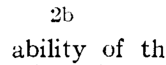
1a



1b



2a



2b

shifts thus are a measure of the ability of the aromatic system to take up the − and + charges. The pertinent vibrational frequencies for the aromatic derivatives in 0.02 molal carbon tetrachloride solution are given in Table II, along with values for the corresponding aliphatic derivatives, methanol, acetaldehyde, acetone and methyl acetate.

In Fig. 3, these frequencies are plotted against the number of aromatic rings in the system to which the substituent is attached; the values for α- and β-naphthalenes are averaged. It is evident that the frequencies rapidly approach a minimum value

Table II

The Effect Upon Hydroxyl and Carbonyl Vibrational Frequencies of Conjugation with Aromatic Ring Systems in Monosubstituted Derivatives, in Carbon Tetrachloride Solution

Substituent	Methane,[a] cm.$^{-1}$	Benzene, cm.$^{-1}$	α-Naphthalene, cm.$^{-1}$	β-Naphthalene, cm.$^{-1}$	9-Phenanthrene, cm.$^{-1}$
OH	3645	3628	3618	3618	3605
CHO	1735	1708	1700	1702	1698
$COCH_3$	1719	1693	1685	1685	1685
$COOCH_3$	1745	1730	1724	1726	1724

[a] Stock samples of these aliphatic derivatives were used.

with increasing number of fused aromatic rings, particularly for the carbonyl-containing substituents; thus, the frequencies in the phenanthrene derivatives are only slightly less than for the naphthalenes. This effect may be interpreted as a direct consequence of the general rule that the importance of an ionic canonical form decreases with increasing charge separation. Upon comparing the possible forms (2b) for say benzaldehyde, naphthaldehyde and 9-phenanthraldehyde, it is apparent that conjugation of the carbonyl group with each additional ring requires canonical forms with increasing charge separation and hence of less importance, so the effects of conjugation approach a limit. The slightly lower carbonyl frequencies in the α-naphthalene derivatives compared to the β-naphthalenes in Table II have a similar interpretation; one of the five ionic forms (2b) of the α-naphthalenes has less charge separation than in the β-naphthalenes, so the conjugation is slightly greater in the α-naphthalenes.[14]

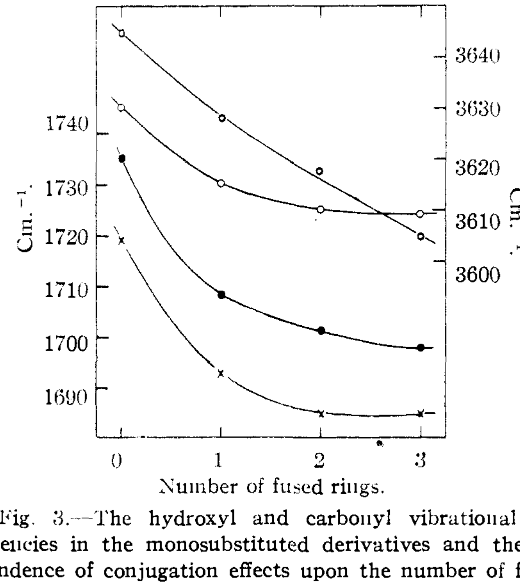


Fig. 3.—The hydroxyl and carbonyl vibrational frequencies in the monosubstituted derivatives and the dependence of conjugation effects upon the number of fused rings in the aromatic ring system: -□-, hydroxyl derivatives; -O-, methyl esters; -●-, aldehydes; -×-, methyl ketones.

In the case of the hydroxyl derivatives, the decrease in the OH stretching frequency with increasing number of rings in the aromatic system appears to be appreciable even upon going from the

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(14) For a summary of other experimental evidence supporting this conclusion, *cf.* G. M. Badger, R. S. Pearce and R. Pettit, *J. Chem. Soc.*, 1112 (1952).

naphthols to 9-phenanthrol. However, the experimental error is larger ($\pm$ 5 cm.$^{-1}$) in the 3μ region than in the 6μ region, so the shape of the curve in Fig. 3 connecting the data on the hydroxyl compounds is qualitative only. It may be significant that conjugation of the hydroxyl group (1b) requires a smaller separation of charge from the ring system than does conjugation of the carbonyl group (2b).

Perhaps the most striking results are obtained from a consideration of all of the $\Delta\nu$(C=O) values determined thus far. These values are summarized in Table III and are presented graphically in Fig. 4. In this figure, the $\Delta\nu$(C=O) values are plotted against Pauling's[4] fractional double-bond characters, neglecting ionic and Dewar forms, for the 3,2-naphthalene bond (1/3), the benzene bond (1/2), the 1,2-naphthalene bond (2/3) and the 9,10-phenanthrene bond (4/5). It is found that the data fall upon straight lines going through the origin. The points for the corresponding hydroxy ketones and hydroxy esters are within experimental error of each other, while the hydroxy aldehydes have consistently lower values of $\Delta\nu$(C=O). It does not seem safe to conclude that the chelation is weaker in the latter case, because $\Delta\nu$(OH) for salicylaldehyde is greater than $\Delta\nu$(OH) for methyl salicylate.[2]

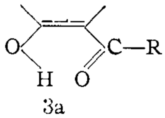
TABLE III

SUMMARY OF $\Delta\nu$(C=O) VALUES FOR BENZENE, NAPHTHALENE AND PHENANTHRENE DERIVATIVES

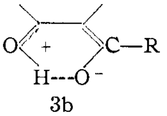
Bond	Aldehydes, cm.$^{-1}$	Ketones, cm.$^{-1}$	Esters, cm.$^{-1}$
3,2-Naphthalene	27[a]	28	32[a]
Benzene	38	45	47
1,2- and 2,1-Naphthalene[b]	51	57	62
9,10-Phenanthrene	61	75	75

[a] Values changed slightly from reference 2 on basis of replotting. [b] Averaged for the two isomers; the bands reported at about 1637 cm.$^{-1}$ in Table I, reference 2, for the hydroxynaphthaldehydes are probably C=C vibrational bands and are not included in these values.

An approximate relation between $\Delta\nu$(C=O) and the double-bond character of the aromatic ring band can be derived in a manner similar to the relation between interatomic distance and double-bond character.[15] The $\Delta\nu$(C=O) values may be considered to depend upon the relative importance of the forms 3a and 3b in the chelated, conjugated



3a



3b

molecule. The potential function for the carbonyl vibration in the hybrid of 3a and 3b is then

$$V(r) = {}^1/_2\{xk_1 + (1 - x)k_2\}r^2 \qquad (1)$$

where r is the vibrational displacement coördinate; k_1 is the carbonyl force constant in 3b; k_2, that in 3a; and x is the fractional contribution of form 3b to the actual structure. Now $\Delta\nu$(C=O) = ν (unchelated) − ν (chelated), and introducing the equation between vibrational frequency and force constants, $\nu = (k/\mu)^{1/2}$, where μ is the reduced mass of the vibrating system, assumed to be the same in 3a and 3b, we have

$$\begin{aligned}\Delta\nu(\mathrm{C{=}O}) &\equiv \nu_u - \nu_c = \nu_u - \{(xk_1 + (1 - x)k_2)/\mu\}^{1/2} \quad (2)\\ &= \nu_u\,\{1 - (1 - (1 - x(1 - k_1/k_2))^{1/2}\}\\ &\cong \nu_u\,(1 - k_1/k_2)\,x/2\end{aligned}$$

The mathematical approximation in the last step is a good one if $x(1 - k_1/k_2)$ is small, which it is since the maximum value of $\Delta\nu$(C=O) is 75 cm.$^{-1}$ while ν_u is around 1700 cm.$^{-1}$. Equation 2 predicts a linear relationship between $\Delta\nu$(C=O) and x. It appears reasonable that the value of x, the fractional contribution of form 3b to the actual structure, should itself be linearly proportional to the availability of π-electrons in the carbon–carbon bond in the ring system. In fact such a conclusion is required by the observed linear relation between $\Delta\nu$(C=O) and the double-bond character of the aromatic ring bond.

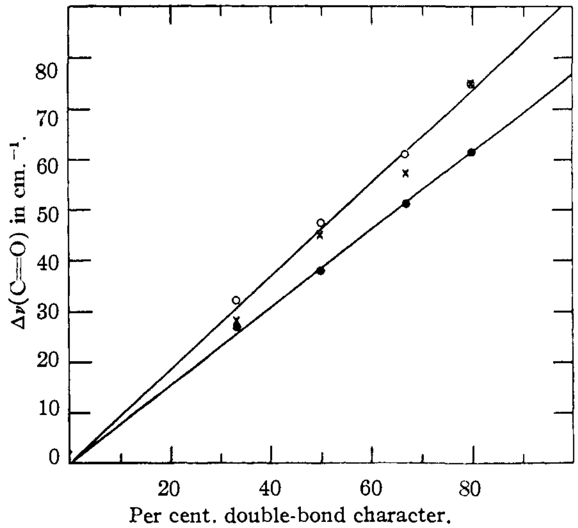


Fig. 4.—Relation of infrared data to aromatic bond character: -○-, hydroxy methyl esters; -●-, hydroxy aldehydes; -×-, hydroxy methyl ketones.

Equation 2 can be used to estimate the magnitude of x. The ratio k_1/k_2 is probably somewhere between 1/2 and 1/3 since the bonds in question are approximately single and double bonds. Accordingly, in the 9,10-phenanthrene derivatives, x is approximately 13–18%, the maximum for the compounds investigated.

Conjugated chelation has been observed also in olefinic compounds such as the acyclic[16] and cyclic[17] enolizable β-keto esters, in which under various conditions the chelation produces carbonyl frequency shifts of from 60 to 90 cm.$^{-1}$. In order to obtain a $\Delta\nu$(C=O) value for a typical olefinic hydrocarbon, comparable to those for the aromatic compounds, we examined the infrared spectra of methyl crotonate (an ester derivative of propylene) and methyl acetoacetate (in the enol form a hydroxy ester derivative of propylene) in 0.02 molal solutions in carbon tetrachloride. The absorption bands observed in the 6μ region and their assignments are listed in Table IV. The methyl

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(15) Reference 4, p. 171.

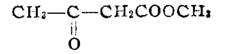
(16) R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

(17) N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Petersen, *ibid.*, **74**, 4070 (1952).

acetoacetate has bands characteristic of the keto form and also the conjugated, chelated enolic form. The effect of chelation upon the ester carbonyl frequency, that is, the Δν(C=O) value, is found to be 71 cm.$^{-1}$. By reference to Fig. 4, this frequency shift in an aromatic system would correspond to 80% double-bond character, although the olefinic bond in propylene might be expected to have more nearly 100% double-bond character since ionic structures were neglected in constructing Fig. 4. At present, we can only speculate about this apparent anomaly which indicates an appreciable difference between the olefinic and aromatic systems. However, it appears likely that part of the difference may arise from differential effects associated with conjugation of the carbonyl group with the aromatic and olefinic systems. In any event, although the results for the aromatic compounds may not be applied simply to olefinic compounds, it appears that the double-bond character in other aromatic systems may be evaluated conveniently by determining a Δν(C=O) value and comparing it with Fig. 4. Such an extension of the present work is now in progress in these laboratories.

Table IV

Infrared Spectra at 6μ of Methyl Crotonate and Methyl Acetoacetate, in 0.02 Molal Carbon Tetrachloride Solution

$CH_3CH{=}CH{-}COOCH_3$		 $CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2COOCH_3$	
1726 cm.$^{-1}$	conj. ester C=O	1751 cm.$^{-1}$	ester C=O
		1726	keto C=O
		1655	conj. chelated ester C=O
1655	conj. C=C	1632	conj. chelated C=C

Experimental[18]

Some of the **9-phenanthrol** (IV) was prepared from purified[19] phenanthrene, but our average yield (three runs) was only 12% as compared to the reported[20] 28–30% (based in each case on phenanthrene consumed). The spectral sample of IV was obtained by demethylating[20] pure 9-methoxyphenanthrene and subliming the recrystallized product three times at 140–145° and 0.2 mm.; m.p. 149–152.1°; lit. m.p. 153–155°.[20,21] This phenol was not soluble enough in carbon tetrachloride to give a 0.02 molal solution. **9-Methoxyphenanthrene** (X), m.p. 93–94°[22] (recrystallized), was prepared in 36% yield (average of five runs) from 9-fluorenone[21] and also in high yield from 9-phenanthrol (IV).[23] Distilled and twice recrystallized **methyl 9-phenanthryl ketone**[24] very slowly sublimed at 73–75° and 0.07–0.08 mm.; white crystals, m.p. 72.9–73.3°; lit. m.p.'s: 73–74°[24]; 74–74.5°.[25] Twice recrystallized **9-phenanthrenecarboxaldehyde**[26] sublimed at 95–98° and 0.07 mm.; m.p. 102.2–103.0°; lit. m.p. 100.5–101°.[26] Twice recrystallized **methyl 9-phenanthrenecarboxylate**[27] sublimed very slowly at 115–120° and 0.5–0.8 mm.; white crystals, m.p. 114–115.8°; lit. m.p. 116°.[27]

10-Hydroxy-9-phenanthryl methyl ketone[10] was recrystallized three times; fine, pale yellow needles, m.p. 97.0–97.7°; wet m.p. 94.2–94.6°; lit.[10] m.p.'s 96° and 101.5–102°, respectively, for two different modifications of this compound.

10-Methoxy-9-phenanthrenecarboxaldehyde (IX).—Literature directions[11] for preparing 2-methoxy-1-phenanthrenecarboxaldehyde were followed. Thus, 5.0 g. of 9-methoxyphenanthrene produced a crude tan solid which was recrystallized (Norit) from ethanol containing a little water to yield 3.0 g. of aldehyde, m.p. 78–81°.[22] Dilution of the mother liquor afforded another 2.0 g., m.p. 75–80°[22] (sintering at 60°); total yield 5.0 g. (88%). Another recrystallization of the larger fraction gave the pure aldehyde as brownish-yellow needles, m.p. 80.5–81.5°[22]; lit. m.p. 79–81°.[10] Essentially the same results were obtained when the period of heating at 80°[11] was increased from two to two and one-half and then to three hours.

10-Hydroxy-9-phenanthrenecarboxaldehyde (V). (a) From **9-Methoxyphenanthrene**.—A mixture of 4.25 g. of N-methylformanilide and 5.25 g. of phosphorus oxychloride was allowed to stand one-half hour at room temperature and then was poured over 2.5 g. of 9-methoxyphenanthrene. After heating for three hours in an oven at 70°, the dark red mixture was decomposed in ice-water. The resulting tan powder was purified by dissolving it in 80 ml. of hot ethanol followed by reprecipitation at room temperature by the slow addition of about 20 ml. of water. The tan to orange crystals (2.6 g.) melted at 83–85°[22] (softened at 75°). Since this material was believed to be mostly unchanged 9-methoxyphenanthrene, it was retreated as before with N-methylformanilide (4.25 g.) and phosphorus oxychloride (5.25 g.) and heated for five hours in an oven at 75°. After decomposition as before, the brown solid was dissolved in 80 ml. of boiling ethanol. On boiling for 25 minutes the brown solution turned green, and most of the hydroxy aldehyde appeared to precipitate. After cooling overnight in a refrigerator, 2.0 g. of light-green crystals, m.p. 133–137°,[22] were obtained which showed only a very faint positive Beilstein test for halogen. This sample was further purified by dissolving it in a mixture of 80 ml. of ether and 100 ml. of ethanol, boiling until precipitation started, slowly cooling to room temperature, and chilling overnight in a refrigerator to yield 1.9 g. (70%) of yellow-green crystals, m.p. 134–135.5°.[22] The spectral sample was prepared by another recrystallization from ethanol followed by sublimation at 135° and 0.25 mm.; pale yellow solid, m.p. 136.7–137.5°; lit. m.p. 133–134°[10]; **anil**, bright yellow, long, fluffy needles, m.p. 161.5–163°; lit. m.p. 160–161°.[10]

In an attempt to prepare the hydroxy aldehyde (V) from 9-methoxyphenanthrene by using one longer heating period at 75°, only a small amount of V was obtained, indicating that some V is formed in the first step of the two-step preparation.

The recrystallized *neutral* portion of the reaction product from a two-step preparation yielded a halogen-containing solid, m.p. 110–130°, which, since it gave V on further purification, may have been a complex of V and phosphorus oxychloride.

(b) From **Preformed 10-Methoxy-9-phenanthrenecarboxaldehyde** (IX).—On heating 1 g. of the preformed methoxy aldehyde for five hours at 75° with 2.1 g. of phosphorus oxychloride and 1.7 g. of N-methylformanilide, 0.7 g. (90%) of recrystallized V, m.p. 135–136°,[22] was obtained.

(c) **Unsuccessful Preparations** (1).—10-Methoxy-9-phenanthrenecarboxaldehyde (1.18 g.), m.p. 80.5–81.5°,[22] was refluxed for two hours in 10 ml. of acetic acid and 3 ml. of 48% hydrobromic acid. The solid obtained on addition of water was dissolved in 200 ml. of boiling alcohol (Norit). Two recrystallizations of the solid obtained by addition of water to the concentrated filtrate gave 0.11 g. of purplish needles, m.p. 136–140°[22] (sintered at 130°); mixed m.p. with authentic 10-hydroxy-9-phenanthrenecarboxaldehyde (m.p. 135–136°[22]) was 107–111°.[22] Recrystallization from benzene–petroleum ether then afforded a small amount of 9-phenanthrol, m.p. 145–149°[22] (sintered at 140°); mixed

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[18] All boiling points are uncorrected; all melting points are corrected unless specified otherwise.

[19] C. A. Dornfeld, J. E. Callen and G. H. Coleman, *Org. Syntheses*, **28**, 19 (1948).

[20] L. F. Fieser, R. P. Jacobsen and C. C. Price, This Journal, **58**, 2163 (1936).

[21] R. F. Schultz, E. D. Schultz and J. Cochran, *ibid.*, **62**, 2902 (1940).

[22] Uncorrected.

[23] H. Gilman and T. H. Cook, This Journal, **62**, 2813 (1940).

[24] J. E. Callen, C. A. Dornfeld and G. H. Coleman, *Org. Syntheses*, **28**, 6 (1948).

[25] E. Mosettig and J. van de Kamp, This Journal, **55**, 3442 (1933).

[26] E. Mosettig and J. van de Kamp, *ibid.*, **55**, 2995 (1933); E. Mosettig in "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 369–370.

[27] E. Mosettig and J. van de Kamp, This Journal, **52**, 3704 (1930).

m.p. with authentic 9-phenanthrol (m.p. 151.5–153.5°[22]) was 145–150°[22] (sintered at 140°). Essentially the same results were obtained on repeating this reaction. Presumably the hydroxyaldehyde first formed and then decarbonylated like the vinylogous formic acid.

(2).—An attempted saponification of the methoxy aldehyde (IX) produced a yellowish oily material which we were unable to purify. Hence, IX apparently did not behave like the vinylogous methyl formate.

Decarbonylation of 10-Hydroxy-9-phenanthrenecarboxaldehyde.—The hydroxyaldehyde (1.11 g.), m.p. 134–135.5°,[22] was refluxed for two hours in 18 ml. of acetic acid and 4 ml. of 48% hydrobromic acid. After cooling and adding 15 ml. of water, the black-red precipitate was boiled in 50 ml. of benzene, and 0.25 g. of unidentified solid was filtered from the hot solution. Concentration of the filtrate to 20 ml. followed by addition of 20 ml. of low-boiling petroleum ether to the boiling solution afforded 0.55 g. (60%) of 9-phenanthrol, m.p. 140–151°[22] (mostly at 148–151°), which was identified by conversion in 67% yield to its acetate, m.p. 76–79°[22]; lit. m.p. 77–78°.[28]

10-Methoxy-9-phenanthrenecarboxylic Acid (VII).—10-Methoxy-9-phenanthrenecarboxaldehyde (0.5 g.), oxidized[10] in aqueous acetone at 50° with 0.625 g. of potassium permanganate, yielded 0.2 g. (40%) of white crystals, m.p. 113–114.5°[22]; lit. m.p. 113°.[10] Two other oxidations yielded essentially the same results.

An attempted demethylation of the methoxy acid with fuming sulfuric acid[29] produced an oil which was not identified.

Methyl 10-Methoxy-9-phenanthrenecarboxylate (VI).—Esterification of 0.47 g. of the methoxy acid (m.p. 110–113°[22]) with diazomethane produced 0.48 g. (94%) of crude methyl ester. Two recrystallizations from low-boiling petroleum ether afforded the pure ester, m.p. 53.2–54.8°, transparent diamond-shaped plates.

Anal.[30] Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.29. Found: C, 76.67, 76.45; H, 4.85, 4.82.

Methyl 10-Hydroxy-9-phenanthrenecarboxylate (III).—A flask equipped with a reflux condenser and containing 0.37 g. of the methyl ester of the methoxy acid and 3.0 g. of crushed anhydrous aluminum chloride (C.P.) in 35 ml. of dry thiophene-free benzene was placed in an oil-bath preheated to 50°. Over the next 80 minutes the bath temperature was raised gradually to 85°. The benzene gently refluxed during the last ten minutes of heating. Gas evolution (methyl chloride) commenced at 60°, proceeded steadily at 68°, and had almost completely tapered off at 72°. The cooled mixture was poured into ice and dilute hydrochloric acid, the organic layer was separated, and the aqueous layer was extracted with ether. The combined ether-benzene solution was washed free of acid and extracted with 5% aqueous sodium hydroxide. Acidification of the alkaline extract produced 0.23 g. (66%) of faintly tan solid, which was identified as the hydroxy ester by its insolubility in 5% aqueous sodium bicarbonate and by the production of a deep blue-green color when ferric chloride was added to its solution in methanol. This was dissolved in 65 ml. of boiling hexane and a very small amount of unidentified tan solid, m.p. 117–125° (to a dark red melt), was filtered from the cold solution. The hexane was evaporated and the residue crystallized twice by dissolving it in methanol at room temperature and cooling the solution in a refrigerator. The pure hydroxy ester formed white needles, m.p. 90.6–91.2°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.55, 76.86; H, 4.84, 5.17.

Attempted Preparations of 10-Hydroxy-9-phenanthrenecarboxylic Acid. (a) Carbonation of 9-Phenanthrol.—Using temperatures of 150–200°, pressures of 300–1600 p.s.i., and reaction periods of 6 to 12 hours, five attempts were made to carbonate[31] both 9-phenanthrol (in the presence of potassium carbonate) and its sodium salt. The more mild conditions produced very little reaction, but the more vigorous conditions afforded a product which undoubtedly contained the carbonate of either 9-phenanthrol or the desired hydroxy acid. Acidification resulted in vigorous evolution of carbon dioxide, but what was presumed to be impure 9-phenanthrol was the only material isolated.

(b) Oxidation of 10-Hydroxy-9-phenanthrenecarboxyaldehyde.—Following Pearl's general procedure,[8] except that the oxidation was started at room temperature, 1.56 g. of hydroxy aldehyde and 2.5 g. of potassium hydroxide in 28 ml. of water was treated dropwise with 1.42 g. of silver nitrate in 8 ml. of water. Stirring for one week gave an acidic product which was sublimed twice at 190–195° and 0.1–0.3 mm. to yield diphenic acid, m.p. 226–228°[22] (sintered at 224° with loss of water at 220°); neutral equivalent, 118; mixed m.p. with authentic diphenic acid (m.p. 221–223°[22]) was 221–225°[22] (softened at 220° with loss of water).

(c) Saponification of Methyl 10-Hydroxy-9-phenanthrenecarboxylate.—A solution of 0.132 g. of the methyl ester in 10 ml. of 10% aqueous sodium hydroxide was heated for one-half hour on a steam-bath, cooled to 5°, and cautiously acidified. No gas was evolved, and an almost white solid separated. Since this material was totally insoluble in aqueous sodium bicarbonate, it was believed erroneously that no reaction had occurred. Hence, the product was heated in 15 ml. of refluxing 10% aqueous sodium hydroxide solution.for one hour. On working up the product as before there was obtained 0.081 g. of a light tan, non-acidic solid which slowly melted over a wide temperature range. An unidentified impurity was removed by heating in 5–6 ml. of methanol and filtering the cold solution. Evaporation of the methanol left 0.050 g. (50%) of a light reddish-brown solid, m.p. 151–154°.[22] While a fresh authentic sample of 9-phenanthrol was being prepared for comparison, the m.p. of the above product changed to 146–152°,[22] but vacuum sublimation raised the m.p. to 149.2–154°[22]; the mixed m.p. with authentic 9-phenanthrol (m.p. 151–155°[22]) was 148.5–155.3°.[22]

Infrared Work.—The spectra were observed with a Model 12B Perkin–Elmer spectrometer with sodium chloride optics. Mulls in Nujol were used for the complete spectra of the solids. In addition, 0.02 molal solutions in redistilled Baker and Adamson reagent carbon tetrachloride were examined in the 3 and 6 μ regions to determine the C=O and O-H vibrational frequencies unperturbed by the intermolecular forces in the solids. The $\Delta\nu$(C=O) values were evaluated from the C=O absorption bands in solution.

The frequencies of the C=O absorption bands were determined by reference to the 6 μ atmospheric water vapor absorption. Most of the C=O absorption bands were fairly sharp in solution and could be located quite accurately. The probable error of the data in Tables I, III and IV is about ±2 cm.$^{-1}$.

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(30) All microanalyses were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

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