Molecular Interactions of Asphalt

Tentative Identification of 2-Quinolones in Asphalt and Their Interaction with Carboxylic Acids Present

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The tentative identification of 2-quinolones has been made in a Wilmington (Calif.) asphalt. These compounds, which exist predominantly in the *N*-unsubstituted form, were concentrated in an asphaltic resin fraction and are largely responsible for the 1655 cm^{-1} infrared absorption band in the asphalt. A strong hydrogen-bonding association between the 2-quinolones and carboxylic acids in asphalt is reported. The association complexes between the 2-quinolines and the carboxylic acids in asphalt and between the model compounds 2-quinolone and cyclohexanecarboxylic acid were studied by infrared spectrometry using a silylation reaction in which the 2-quinolones and carboxylic acids reacted at different rates. The ability of two solvents, methylene chloride and tetrahydrofuran, to break up hydrogen-bonded molecular complexes is shown. The diagnostic value of these solvents in infrared spectrometry for identification of carbonyl functional group types has been demonstrated, and use of these solvents for molecular association studies in asphalts is reported.

THE CARBONYL STRETCHING region of the infrared spectra of asphalts (approximately 1620–1800 cm^{-1}) is generally broad and irregular in shape and has not been exploited in asphalt composition studies. The lack of exploitation of this region probably results from the complexity of the absorption bands caused by the presence of a large variety of functional groups. These groups are polar; and many are capable of forming intermolecular complexes, often through hydrogen bonding, thus further complicating the spectra. Intermolecular hydrogen bonding in asphalts has been studied in the hydrogen-stretching region of the infrared spectra at 3100–3700 cm^{-1} (*1*) but has not been related to interactions involving the carbonyl group. In the present study, molecular complexes formed through hydrogen bonding interactions to carbonyl groups are reported. The complexity of asphalt precludes, from a practical standpoint, the possibility of isolating the compounds containing these interacting groups; therefore it is necessary to devise techniques to study specific functional group types in the presence of many others. We have followed this approach by applying selective chemical reagents and solvents capable of forming association complexes to asphalt fractions and interpreting the results using infrared spectrometry.

Most asphalts show a major band maximum in the infrared spectra at about 1700 cm^{-1} which has been attributed to the carbonyl group absorption of such functional groups as carboxylic acids, acid anhydrides, ketones, esters, etc. (*2–5*). In many asphalts, however, an absorption in the carbonyl region centered at about 1655 cm^{-1} is observed. This band varies widely in intensity in different asphalts and is absent in some. The band was reported by Stewart (*6*) in an asphaltic resin fraction, and he suggested that it might result from amides or amines, although no attempt was made to confirm the speculation. The band at 1655 cm^{-1} is difficult to observe because in many instances it is overlapped on one side by the carbonyl absorption centered at 1700 cm^{-1} and on the other by the so-called aromatic band at about 1600 cm^{-1}.

In the present paper we report that 2-quinolones and their association complexes with carboxylic acids have tentatively been identified as major contributors to the 1655 cm^{-1} band in asphalts. 2-Quinolones have been identified in the high-boiling fractions of petroleum crude oils (*7, 8*), and the carboxylic acids in petroleum have received considerable study (*9*). However, 2-quinolones have not previously been identified in asphalts nor has their association with carboxylic acids been recognized. 2-Quinolones in asphalt and their interaction products with the carboxylic acids present were studied in this work by selectively silylating the quinolones and carboxylic acids. Similar studies were conducted on the model system, 2-quinolone and cyclohexanecarboxylic acid. The effects of associating solvents on the acid–quinolone interactions; on the interactions of carbonyl groups in an asphalt fraction; and on the carbonyl stretching frequencies of model acids, esters, ketones, and amides were also studied.

Because the molecular interactions of 2-quinolones and carboxylic acids with themselves and with each other result from strong hydrogen bonds (*10*), the probable importance of these interactions as significant contibutors to asphalt physical properties is suggested.

EXPERIMENTAL

Materials. Three asphaltic samples were used in the analytical work: Wilmington (Calif.) asphalt described in previous studies (*1, 11, 12*), a molecular distillation fraction from this asphalt (*4*), and an asphaltic resin fraction obtained by the Kleinschmidt (*13*) separation procedure from the molecular distillation fraction. The asphaltic resin fraction from the Kleinschmidt procedure is that portion of deasphaltened asphalt not removed from fuller's earth with pentane or methylene chloride (CH_2Cl_2) but removed with methyl ethyl ketone. The molecular distillation fraction,

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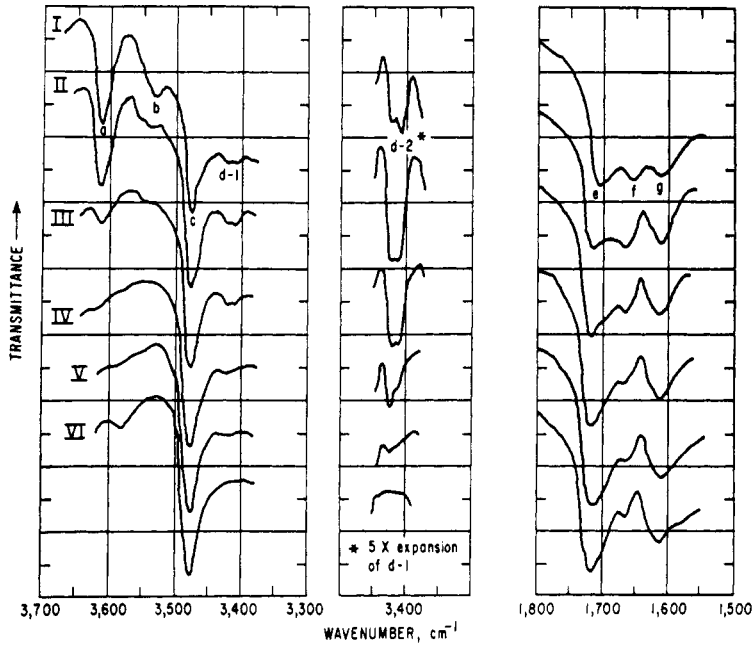


Figure 1. Infrared spectra during silylation of asphaltic resins from molecular distillation fraction, Wilmington asphalt

0.10 g/15 ml in CCl_4, 3600–3400 cm^{-1} region in 1.06-cm cell, 1800–1600 cm^{-1} region in 0.10-cm cell, solvent and reagent compensated; Curve I, before addition of HMDS; II, 1 hr at 25 °C after addition of HMDS; III, an additional 18 hr at 46 °C; IV, V, VI, an additional 30 min, 30 min, and 7 hr at 72 °C, respectively

which had an average molecular weight of 710 (vapor pressure osmometry in carbon tetrachloride), was distilled from the whole asphalt and represented 6.4% of the charge. Thirty per cent of the molecular distillation fraction appeared as asphaltic resins. Hexamethyldisilazane, HMDS, [bis(trimethylsilyl)amine] used in the silylation reactions was from Pierce Chemical Co. The carbon tetrachloride (CCl_4) and methylene chloride (CH_2Cl_2) were Baker and Adamson ACS reagent grade. Tetrahydrofuran (THF) was from Eastman Chemical Co. and was stabilized with 0.025% butylated hydroxytoluene. The small amount of stabilizer caused no significant interference in the infrared spectra. For use as a spectral solvent, THF must be free of hydroperoxides which, if present, spontaneously decompose at the slightly elevated temperatures in the infrared cell and give rise to spurious carbonyl absorption bands. Cyclohexanecarboxylic acid was Eastman Practical grade, and 2-quinolone was Eastman white label; each was of better than 95% purity. Materials used to determine the carbonyl frequencies of the infrared spectra of the model compounds were obtained from laboratory supply houses and were of unknown purity.

Infrared Spectra. Infrared spectra were obtained on a Perkin-Elmer Model 521 infrared spectrophotometer. Solutions from the silylation experiments were examined directly without solvent removal in 1.06-cm (NH and OH region) and 0.1-cm (carbonyl region) cells equipped with potassium bromide windows. The spectrum of excess HMDS was nulled by a CCl_4 solution of the reagent in a variable path-length cell placed in the reference beam. Scale expansion (5×) was used where necessary is observing weak absorption bands. Solution concentrations used are noted on the respective figures showing the spectra. Conditions under which the spectra of the model carbonyl compounds and the molecular distillation fraction were obtained are noted in the corresponding table and figures.

Silylation Reaction. Asphalt or asphaltic resins (0.1 g/15 ml) or a mixture of 2-quinolone and cyclohexanecarboxylic acid (5 mg and 20 mg, respectively, per 100 ml) was dissolved in CCl_4. To 15 ml of the above solution was added 0.15 ml of HMDS, and the mixture was allowed to stand at room temperature, warmed, or refluxed as described later. Samples (cooled when necessary) were transferred from the reaction flask directly to the infrared cell for determination of the infrared spectra.

RESULTS AND DISCUSSION

The 1655 cm^{-1} infrared absorption band is weak in most asphalts and occasionally missing or barely discernible in others. Consistent with Stewart's observation (*6*), we found that the types of compounds in asphalt which absorb in this region are concentrated in the asphaltic resins. The 1655 cm^{-1} absorbing material can also be concentrated from a molecular distillation fraction of asphalt by elution from a silica gel column (*5*) with benzene–methanol (1:1) following prior elution of the column with benzene. The silylation studies reported in this paper were conducted on asphaltic resins separated on fuller's earth; however, confirming experiments were run on asphaltic resins from silica gel and on several whole asphalts, including the asphalt from which the asphaltic resins were derived.

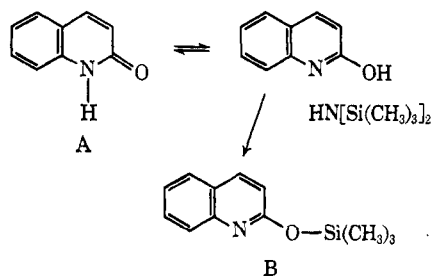
Evidence for 2-Quinolone in Asphalt. Several preliminary chemical tests were run on a sample of asphaltic resins to classify the functional group type giving rise to the 1655 cm^{-1} band. The band was not affected by attempted hydrolysis with either 10% sodium hydroxide or 10% hydrochloric acid. No reduction occurred using zinc and 10% sodium hydroxide, but reaction with lithium aluminum hydride removed the 1655 cm^{-1} band. These tests indicate that the 1655 cm^{-1} band results from a carbonyl functional group which is resistant to hydrolysis and to all but vigorous reduction conditions. 2-Quinolones exhibit chemical properties similar to those indicated by the classification tests and, further, show strong carbonyl absorption bands in the 1655 cm^{-1} region.

On the assumption that the compound type, of which 2-quinolone is typical, might be responsible for the 1655 cm^{-1} band in asphalts, the compound 2-quinolone was chosen as a model compound for study in this work. 2-Quinolone rather than 2-pyridone, which has similar properties, was chosen as a model compound because it is likely that 2-quinolones would predominate over the lower molecular weight 2-pyridones in a high-molecular-weight petroleum residue like asphalt. Copelin's (*7*) identification of 2-quinolones in heavy gas oil supports this assumption. Infrared spectra of the functional groups

and thermodynamic data of 2-pyridone (*14*) and 2-quinolone (*10*) are quite similar, and conclusions based on the chemical reactivity and interactions of one should apply generally to the other.

Further evidence suggesting that the 1655 cm^{-1} band in asphalt might result from 2-quinolones was obtained by comparing the spectra of pure 2-quinolone with the spectra of asphaltic resins in the NH-stretching region. The free NH band of 2-quinolone appears at 3408 cm^{-1} in CCl_4 solution but is weak even in highly dilute solutions, and its intensity is concentration dependent because of strong intermolecular hydrogen bonding (*10*). Asphaltic resin also shows a weak band at about 3410 cm^{-1} which is also concentration dependent, indicating a hydrogen capable of hydrogen bonding.

With indirect evidence suggesting 2-quinolones and because of the near impossibility of isolating pure compounds from asphalt, specific reactions were sought by which this compound type could be confirmed in the presence of the many other functional types present. 2-Quinolone (A) was found to react with silylating reagents such as hexamethyldisilazane (HMDS) through its hydroxy tautomer to yield a silyl ether (B) as follows:



A similar reaction with 2-pyridone has been reported (*15*). The reaction is easily followed by infrared spectrometry because both the NH and carbonyl absorptions disappear simultaneously upon silylation.

Results of the application of the silylation reaction to the asphaltic resin fraction from a Wilmington (Calif.) asphalt molecular distillation fraction are shown in the series of spectra reproduced in Figure 1. Spectrum I of Figure 1 shows the absorption bands of interest in the unreacted resins. Bands previously assigned are the free phenolic OH (*1*) at 3610 cm^{-1} (*a*), the free carboxylic acid OH (*16*) at 3540 cm^{-1} (*b*), the free pyrrolic-type NH (*1*) at 3480 cm^{-1} (*c*), the carbonyl group (*6*) at about 1700 cm^{-1} (*e*), and the so-called aromatic band (*6*) at about 1600 cm^{-1} (*g*). Band *d*-2 is a 5× expansion of band *d*-1 and is a doublet with frequencies at about 3410 and 3422 cm^{-1}. Band *f* is the 1655 cm^{-1} band discussed previously. Upon addition of HMDS to the asphaltic resin solution (spectrum II), band *b* rapidly decreased accompanied by a significant increase in band *d*-2. Also noted was an apparent increase in frequencies of bands *e* and *f* and an increase in the valley between bands *f* and *g*. After 18 hour at 46 °C (spectrum III), band *b* nearly disappeared, band *a* decreased considerably, and bands *d*-2 and *f* began to decrease. Spectra IV, V, and VI show that with the increasing temperature and reaction times indicated in the figure, bands *d*-2 and *f* decreased simultaneously, leaving only a small band at *f* which was resistant to further change after the disappearance of band *d*-2.

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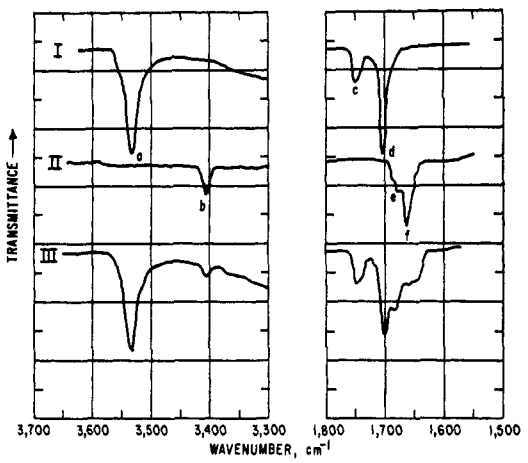


Figure 2. Infrared spectra of cyclohexanecarboxylic acid (I), 2-quinolone (II), and their mixture (III)

I, 20.0 mg/100 ml; II, 5.0 mg/100 ml; III, 20.0 mg I and 5.0 mg II in 100 ml; all solutions in CCl_4, 3600–3400 cm^{-1} region in 1.06-cm cell, 1800–1600 cm^{-1} region in 0.10-cm cell, solvent compensation

These silylation results are interpreted as follows: upon addition of HMDS to the asphaltic resins, the carboxylic acids are rapidly silylated at room temperature, yielding the silyl ester of the acid. This results in the disappearance of the free acid OH band (*b*) and the formation of a silyl ester carbonyl band which has a slightly higher frequency than the bonded acid carbonyl. The formation of the silyl ester carbonyl band causes the apparent increase in frequency of the 1700 cm^{-1} band (*e*). Silylation of the phenols results in a decrease in the free phenolic OH band (*a*). The disappearance of the phenolic and carboxylic acid OH bands in asphalt upon silylation has previously been reported by this laboratory (*16*). Silylation of the carboxylic acids also causes the increase in the free NH band (*d*-2) attributed to 2-quinolones through liberation of the 2-quinolones which previously were strongly associated with the carboxylic acids. The increase in the valley between bands *f* and *g* and the increased frequency of band *f* result from loss of the quinolone carbonyl involved in the association complex between the 2-quinolones and carboxylic acids and the corresponding production of quinolone carbonyl which absorbs at a higher frequency. Finally, the 2-quinolones silylate with the simultaneous disappearance of their NH (*d*-2) and carbonyl (*f*) bands. Note that the band at 3410 cm^{-1} silylates at a faster rate than the one at 3422 cm^{-1}, suggesting the presence of at least two structurally different compounds capable of tautomerism. Based on the nearly complete disappearance of bands in the 1655 cm^{-1} region, it is concluded that most 2-quinolones present are *N*-unsubstituted. This is consistent with the work of Copelin (*7*), who concluded that over 75% of the 2-quinolones in a gas-oil fraction from a Wilmington crude were *N*-unsubstituted.

The interpretation presented above was tested using the model compounds 2-quinolone and cyclohexanecarboxylic acid, the infrared spectra of which are shown in Figure 2. Spectra I and II are those of the acid and quinolone and show the free OH (*a*) and NH (*b*) bands, the free carbonyl bands (*c* and *e*), and the bonded carbonyl bands (*d* and *f*), respectively. The spectrum of a mixture of 2-quinolone and cyclohexanecarboxylic acid at the same initial concentration (spectrum III) shows decreases in the free NH and OH bands and complex changes in the carbonyl region in which bands attributed to the individual species decrease and additional

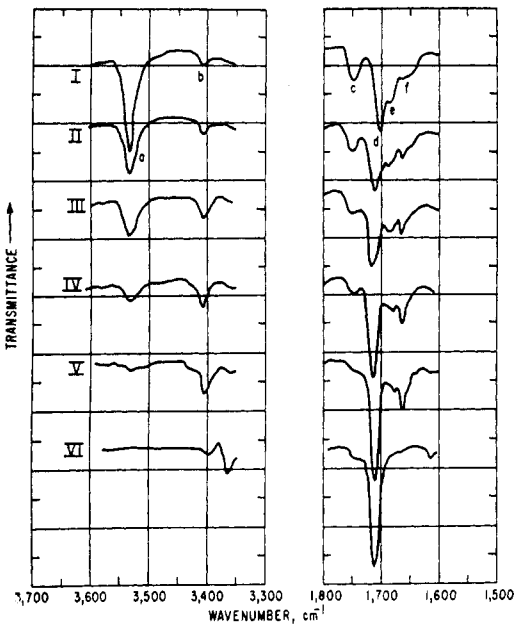
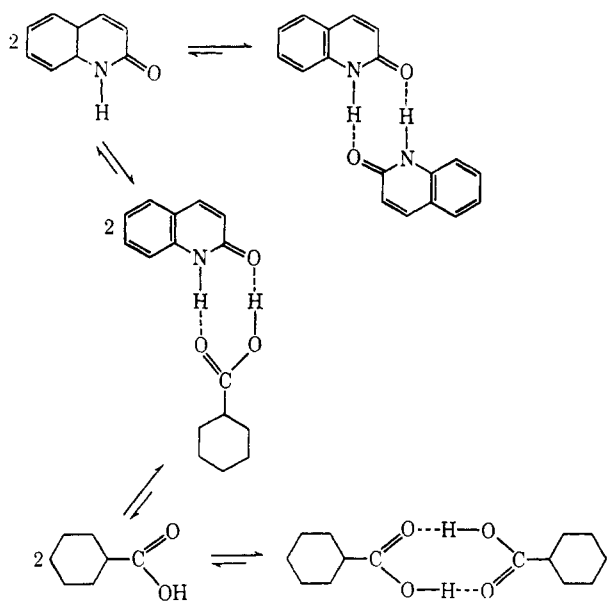


Figure 3. Infrared spectra during silylation of a mixture of 2-quinolone and cyclohexanecarboxylic acid

20.0 mg cyclohexanecarboxylic acid and 5.0 mg 2-quinolone/100 ml in CCl_4, 3600–3400 cm^{-1} region in 1.06-cm cell, 1800–1600 cm^{-1} region in 0.10 cm cell, solvent and reagent compensated; curve I, before additionof HMDS; II, 1 hr at 25 °C after addition of HMDS; III and IV, successive warming to 60 °C for a few minutes; V and VI, an additional 3 min and 15 hr at 72 °C, respectively

bands appear. The complexity of the carbonyl region of the mixture has been shown (*10*) to result from the following equilibria:



Not only do the acid and 2-quinolone strongly self-associate, but they also associate strongly with each other to form a mixed dimer. As a result, the carbonyl region of the spectra is composed of six individual carbonyl bands, some of which are not readily observable because of band overlap. These bands are the free and bonded (dimer) acid bands at 1752 cm^{-1} and 1706 cm^{-1}, the free and bonded (dimer) quinolone bands at 1680 cm^{-1} and 1664 cm^{-1}, and the bonded acid and bonded quinolone bands of the mixed dimer at 1689 cm^{-1} and 1651 cm^{-1}, respectively (*10*).

Changes in the absorption bands on silylation of a model quinolone–acid mixture are shown in Figure 3. Similar to the acids in the resins, the free acid OH of cyclohexanecarboxylic acid silylated rapidly (band *a*), forming the silyl ester (compare with Figure 1). The formation of the ester carbonyl band at 1712 cm^{-1} and the simultaneous loss of the bonded acid carbonyl band *d* appear as an apparent increase in the frequency of the bonded acid carbonyl band (spectra I through IV). As expected, silylation also resulted in the loss of the free acid carbonyl band *c*. Silylation of the carboxylic acid caused an increase in the concentration of free and dimer 2-quinolone as evidenced by an increase in the absorbances of the free NH (*b*) and bonded carbonyl (under *f*) bands. Loss of the bonded acid and 2-quinolone carbonyls involved in the mixed dimer is evidenced by changes in the area of band *e* and loss of the shoulder on the low frequency side of band *f*, respectively. Refluxing the mixture (curve VI) finally caused the 2-quinolone NH (*b*) and carbonyl (*f*) bands to disappear. A mixture of 2-pyridone and cyclohexanecarboxylic acid was found to silylate in a similar manner.

In addition to the evidence already presented for the presence of 2-quinolones in asphalt, their presence in asphalt was also indicated by high-resolution mass spectrometry. Parent peaks characteristic of the unsubstituted 2-quinolone and of substituted 2-quinolones were observed in the asphaltic resin fraction. Moreover, the P − 28 ions were also observed. These ions result from the loss of carbon monoxide from the parent ions as previously described (*17*). This fragmentation is characteristic of the conjugated lactam structure.

Solvent Effects on Molecular Interactions. Because 2-quinolones, carboxylic acids, and possibly other carbonyl-containing molecules in asphalt associate strongly in neat samples and in CCl_4 solutions, their characterization by infrared spectrometry without supplementary chemical evidence is difficult. The infrared spectra are further complicated by the variety of carbonyl types present, thus producing broad carbonyl absorptions composed of many overlapping bands. Figure 4 shows the ability of associating solvents to reduce the complexity of the carbonyl absorption bands of 2-quinolone and cyclohexanecarboxylic acid. Both the acid (I) and quinolone (II) are in equilibrium with their cyclic dimers in CH_2Cl_2 as evidenced by two carbonyl absorptions for each compound. The lower frequency in each case is assigned to the bonded carbonyl of the dimer and the higher frequency to free carbonyl of the monomer. Although these compounds associate in CH_2Cl_2, the tendency to form a cyclic dimer is much less in CH_2Cl_2 than in CCl_4. This can be seen by comparing spectra I, II, and III in Figure 4 with those in Figure 2. The ability of CH_2Cl_2 to reduce the association of carboxylic acids has previously been noted (*4*). Methylene chloride has also been shown to reduce intramolecular hydrogen bonds in certain amides (*18*). The ability of CH_2Cl_2 to reduce association in hydrogen-bonded complexes probably results from the interaction of its electron deficient hydrogens with the hydrogen-bonding bases, thus competing with the bonding hydrogens in the complex. The tendency of halogenated hydrocarbons such as CH_2Cl_2 (*18*), chloroform (*18–20*), and even

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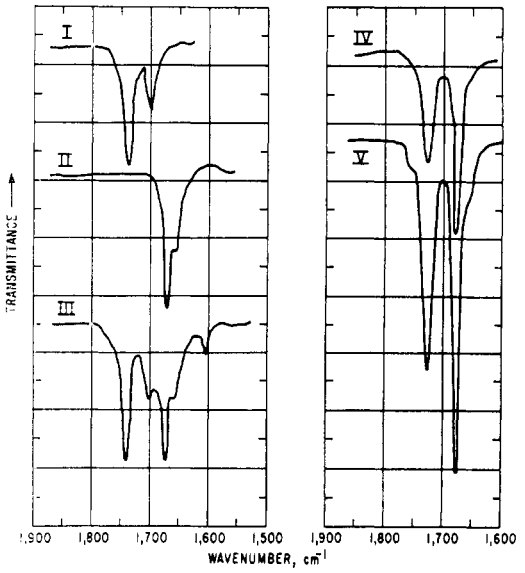

Figure 4. Infrared spectra of cyclohexanecarboxylic acid and 2-quinolone in methylene chloride and tetrahydrofuran

Curves I, II, and III, cyclohexanecarboxylic acid, 2-quinolone, and their mixture, respectively, in CCl_4; Curves IV and V, mixture of cyclohexanecarboxylic acid and 2-quinolone at two concentrations in THF; all spectra are dilute solutions in 0.10-cm cells, concentrations unknown

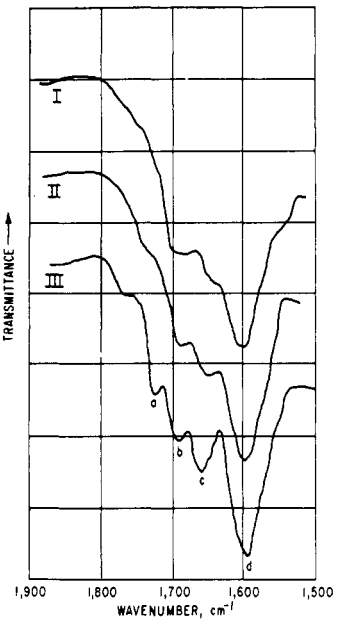

Figure 5. Infrared spectra of molecular distillation fraction from Wilmington asphalt in carbon tetrachloride (I), methylene chloride (II), and tetrahydrofuran (III)

0.1 g/10 ml in 0.05-cm cell, solvent compensated

CCl_4 (*21*), to form association complexes with electron donors has been reported. In spite of the reduced association of 2-quinolone and carboxylic acids in CH_2Cl_2 when compared with CCl_4, the spectrum of the mixture is still complex and overlapped (Figure 4, III) and is composed of the six bands representing the free and bonded carbonyls of the pure compounds plus the bonded carbonyls of the mixed dimer similar to those described for the mixture in CCl_4 solution.

Electron donating solvents such as tetrahydrofuran (THF) have been reported to form 1:1 complexes with electron acceptors (*22*) and to break up molecular associations between the ketone oxygen and the magnesium in chlorophyll-like materials (*23*). The ability of THF to reduce molecular association and thus simplify the carbonyl absorption region in the 2-quinolone–cyclohexanecarboxylic acid mixture is shown in spectra IV and V, Figure 4, in which the spectra at two different concentrations in THF are reproduced. Instead of six carbonyl bands, only two are present. THF completely prevented the association of the acid or quinolone, as either dimer or mixed dimer; and only the free carbonyl bands at 1728 cm^{-1} for cyclohexanecarboxylic acid and 1678 cm^{-1} for 2-quinolone are apparent. This probably results from the strong association of the oxygen of the THF molecule with the bonding hydrogens in the acid and quinolone, thus liberating the carbonyl groups. Any possible equilibrium toward dimer formation is overwhelmed by the preponderance of solvent molecules.

The ability of CH_2Cl_2 and THF to break up the molecular association of carbonyl groups in the molecular distillation fraction from Wilmington asphalt is shown in Figure 5. Spectrum I is a reference trace in CCl_4. Note the broad carbonyl band at about 1700 cm^{-1} and the weak shoulder in the 1665 cm^{-1} region. The spectrum in CH_2Cl_2 (II) shows increased resolution of the 1700 cm^{-1} band with a slight solvent shift to a lower frequency and an increased resolution of the 1655 cm^{-1} region. There is a weak shoulder at about 1720 cm^{-1} which probably results from the free carbonyl of carboxylic acids. Finally, spectrum III shows the absorption bands of the fraction in THF. A strong free carboxylic acid carbonyl band (*a*) is now apparent. Band *b* is probably caused by ketones plus possibly some associated acids, and band *c* is well resolved and probably results primarily from 2-quinolones.

The electron donating ability of THF is further demonstrated by its ability to completely associate with the electron deficient or acidic phenolic OH and pyrrolic NH groups in asphalt. The free phenolic OH and pyrrolic NH bands, normally observed at 3610 cm^{-1} and 3480 cm^{-1} in CCl_4 (*1*), are not observed in THF solutions. These groups both show a broad absorption band of the association complex in THF with a band maximum of about 3300 cm^{-1}. The model compounds phenol and indole both give association bands in THF at the same frequency (3300 cm^{-1}). These results further confirm the previous assignment in asphalts (*1*) of the phenolic OH and pyrrolic NH bands at 3610 and 3480 cm^{-1}, respectively.

Associating solvents such as CH_2Cl_2 and THF can be most useful in the resolution of the carbonyl band; however the asphalt components must be soluble in the THF or CH_2Cl_2 solvent for dissociation of the asphalt molecules to occur. Meaningful resolution of the carbonyl band is complicated by the presence of an increasing number of carbonyl types with differing absorption frequencies. Therefore, the use of associating solvents to simplify the carbonyl region will be less suc-

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Table I. Carbonyl Stretching Frequencies of Selected Classes of Carbonyl-Containing Compounds

Compound	Frequency,[a] cm^{-1} in CH_2Cl_2	in THF	Frequency shift from CH_2Cl_2 to THF
Acids			
Stearic acid	1707 (1742)[b]	1734	−8
Cyclohexanecarboxylic acid	1703 (1740)	1728	−12
Benzoic acid	1692 (1730)	1721	−9
Cholanic acid	1706 (1742)	1731	−11
Esters			
Cyclohexyl acetate	1722	1732	+10
Methyl stearate	1730	1740	+10
Phenyl stearate	1751	1760	+9
Methyl benzoate	1719	1725	+6
Coumarin	1730	1736	+6
Ketones			
Cyclohexanone	1706	1710	+4
Acetophenone	1683	1687	+4
Laurophenone	1682	1686	+4
Benzophenone	1658	1662	+4
Anthrone	1660	1666	+6
Fluorenone	1713	1717	+4
Amides			
1-Naphthylacetamide	1682	1690	+8
Benzamide	1679	1683	+4
n-Methyl-2-phenylacetamide	1667	1680	+13
N,N-Diphenylacetamide	1665	1679	+14
Oxindole	1730 (1710) (1753)	1732	+2
6-Methyl-4-quinolone	1641	1646	+5
2-Quinolone	1673 (1660)	1678	+5
2-Pyridone	1672 (1654)	1678	+6

[a] Spectra are of dilute solutions contained in a 0.05-cm cell using solvent compensation in the reference beam.

[b] Frequencies in parentheses are those of bands of minor intensity. For the acids, this is the free carbonyl band; for 2-quinolone, the associated carbonyl band; and for oxindole, type unknown.

cessful with whole asphalts than with asphalt fractions that are more homogeneous.

To support the interpretation of this work and to provide reference frequencies for future studies of the carbonyl region in asphalt, the infrared spectra of several classes of compounds containing the carbonyl group were obtained in CH_2Cl_2 and THF. Results are shown in Table I. Spectra were obtained in dilute solutions using a 0.05-cm cell and compensating with solvent in the reference beam. In some instances two or more carbonyl bands were observed, and the weaker bands are reported in parentheses. The higher frequencies of the acids and 2-quinolone in CH_2Cl_2 result from the free carbonyls; the lower frequencies result from the bonded carbonyls. The reason for the multiple carbonyl peaks of oxindole is unknown.

Carbonyl solvent shifts on going from CH_2Cl_2 to THF are also shown in Table I. With self-associated species, shifts of the free carbonyl are reported. All classes of carbonyls investigated shifted to a higher frequency on going from CH_2Cl_2 to THF except the carboxylic acids free C=O bond which showed a decrease in frequency. This behavior can be useful in distinguishing between carboxylic acids and ketones formed in asphalt components on oxidative aging. Care must be taken, however, to distinguish between the bonded and free carbonyl bands in CH_2Cl_2. This decrease in frequency of free acid carbonyl in THF probably results from the inductive effect of the strong hydrogen bond formed between the THF and the acid OH group.

Significance of Molecular Interactions in Asphalt. It is tempting to speculate on the significance of the interactions of 2-quinolones and carboxylic acids on the physical properties of asphalts. Upon examination of the 1655 cm^{-1} absorption band in several asphalts, and based on molar absorptivities for 2-quinolone (*10*), it is estimated that the concentration of 2-quinolones in some asphalts may approach 0.5 weight per cent. Carboxylic acids initially present and formed on oxidation by oxidative weathering may exceed this value several fold based on acid numbers determined in our laboratory. Thermodynamic studies of model compounds (*10*) have shown that the equilibrium constants (1 mol at 22 °C in CCl_4) for the self-associations of 2-quinolone and cyclohexanecarboxylic acid and for the association of quinolone and acid to form the mixed dimer are 3.34×10^4, 3.84×10^3, and 2.52×10^4, respectively; hydrogen-bond strengths ($\Delta H°$, kcal/mol dimer) for the respective dimers are −8.69, −11.1, and −10.3. These data show a high degree of association and the formation of strong hydrogen bonds. 2-Quinolones and carboxylic acids in asphalt would be expected to behave similarly. This is evidenced by the infrared spectra of neat asphalt samples which show the 2-quinolones and carboxylic acids to be highly associated. These and other molecular interactions, therefore, must play an important part in determining the rheological or flow properties of asphalt, both initially and as they change during oxidative weathering.

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