203–206°) was reduced with lithium aluminum hydride as described.[11] The 17α-aminomethyl-Δ^5-androsten-$3\beta,17\beta$-diol (ii) (m.p. 215–220°) obtained was treated with NaNO$_2$ in aqueous acetic acid yielding Δ^5-D-homoandrosten-3β-ol-17a-one (iv) (crude m.p. 178–180°). The acetate derived from iv was hydrogenated in the presence of Pt catalyst and the crude product oxidized with CrO$_3$–acetic acid and hydrolyzed with aqueous methanolic potassium carbonate as described,[11] yielding D-homoandrostan-3β-ol-17a-one, m.p. 192–195°, reported m.p. 193–195°.[11]

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The Infrared Spectra of *p*-Benzoquinones

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The infrared spectra of twenty-two *p*-benzoquinones in the region 5 to 15 μ are reported and the relationship between them and the nature of the substituents is discussed.

Several studies have been made of the relationship between the structures of quinones and the location of their carbonyl stretching bands. Flett[1] has examined a number of anthraquinones and Hadži and Sheppard[2] have investigated several polycyclic quinones. Fuson and his school[3–6] have conducted extensive studies of the spectra of a large variety of quinones and have arrived at valuable correlations. This work, however, included consideration of only very few substituted *p*-benzoquinones and was limited to the measurement and discussion of the carbonyl stretching frequencies alone A more specific compilation of the carbonyl stretching frequencies of substituted *p*-benzoquinones has been given by Barchewitz, Tatibouët and Souchay[7] but again no reference was made to other infrared bands. It is the purpose of the present communication to report all the major bands between 5 and 15 μ of a series of twenty-two *p*-benzoquinones and to propose some tentative correlations on the basis of these observations.

Experimental

The quinones were specimens previously prepared in this Laboratory or were purified samples of commercially available materials. The spectra of solutions in carbon disulfide (*ca.* 0.1 *M*) or of mulls in mineral oil were recorded with a Perkin–Elmer Model 21 spectrophotometer using an NaCl prism. The spectra were calibrated by the use of a polystyrene film and atmospheric carbon dioxide.

Results and Discussion

The major bands observed between 5 and 15 μ are recorded in Table I (CS$_2$ solution) and in Table II (solid mull).

It has previously been observed that the spectra of certain benzoquinones[7,8] and naphthoquinones[5,8a] show two bands in the carbonyl stretching region. Our data provide further examples of such splitting of the carbonyl band.[9] It was originally proposed[5] that in the case of the naphthoquinones this phenomenon was due to unsymmetrical substitution giving rise to two non-equivalent resonating carbonyl systems. Subsequently, it was suggested[8a] that a more likely explanation was that the higher wave length band of the two had its origin in a C═C stretching vibration. We also find that the splitting cannot be due solely to the presence of different conjugated carbonyl systems, since no correlation between the symmetry of the quinones and the splitting of their carbonyl bands is apparent in the cases here investigated. However, it appears unlikely that the second bands may be attributed to the C═C vibrations in these cases, at least, since the bands, which occur between 5.97 and 6.14 μ, are at abnormally low wave lengths for such vibrations and also the solid spectra show bands at somewhat higher wave lengths (6.17–6.49 μ) which may readily be interpreted as arising from C═C vibration (*vide infra*). The origin of the splitting remains obscure, as does that of the analogous splitting of the carbonyl bands of some acid chlorides[10]; it may perhaps be due to vibrational interaction effects[2] but requires further study for its elucidation.

A well-defined relationship between the nature of the substituent groups and the position of the carbonyl bands emerges from a consideration of the spectra in both solution and the solid state.[11] The introduction of electron-donating groups, *viz.*, alkyl, methoxyl and hydroxyl, leads to an increase in the wave length of carbonyl absorption, the effect increasing as the number of such substituents becomes larger. Thus, for example, in the series of methyl derivatives 2, 5, 7, 13, 15 and 20, the carbonyl bands occur (i) in CS$_2$ at 6.01, 6.02, 6.02, 6.03, 6.03 and 6.08 and 6.09 μ, respectively, and (ii) in the solid state at 6.01, 6.02, 6.00 and 6.09, 6.05, 6.06 and 6.10 μ, respectively. It is of interest

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[1] M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948).

[2] D. Hadži and N. Sheppard, THIS JOURNAL, **73**, 5460 (1951).

[3] M. L. Josien and N. Fuson, *Bull. soc. chim. France*, 389 (1952).

[4] M. L. Josien and N. Fuson, *Compt. rend.*, **234**, 1680 (1952).

[5] M. L. Josien, N. Fuson, J. M. Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).

[6] N. Fuson. M. L. Josien and E. M. Shelton, THIS JOURNAL, **76**, 2526 (1954).

[7] P. Barchewitz, F. Tatibouët and P. Souchay, *Compt. rend.*, **236**, 1652 (1953).

[8] (a) M. L. Josien and J. Deschamps, *J. chim. phys.*, **52**, 213 (1955); (b) D. J. Cosgrove, D. G. H. Daniels, J. K. Whitehead and J. D. S. Goulden, *J. Chem. Soc.*, 4821 (1952).

[9] It is probable that in other cases splitting occurs but is not detected because the bands lie too close to be resolved under the conditions used. For example, although we and other workers[3–5,7] report a single carbonyl band for *p*-benzoquinone, yet others have observed two bands.[8]

[10] *Cf.*, for example, M. St. C. Flett. *Trans. Faraday Soc.*, **44**, 767 (1948).

[11] It is necessary to consider these independently, since, as has been noted previously with other series of quinones,[3] there is no consistent relationship between these bands in the different states.

TABLE I

SPECTRA OF CS_2 SOLUTIONS OF 1,4-BENZOQUINONES[a]

No.[b]	Substituents				Wave lengths of major infrared bands (μ)[c]
	2	3	5	6	
1	H	H	H	H	**5.99**, 7.38, **7.71**, **9.42**, *10.61*, **11.38**
2	Me	H	H	H	**6.01**, 7.31, 7.48, *7.74*, *7.85*, 8.85, *9.19*, *9.99*, **11.08**, *12.38*
3	Et	H	H	H	**6.02**, 7.42, *7.63*, *7.75*, *7.84*, 8.43, *8.67*, *9.16*, 9.59, **11.03**, *12.04*
4	Cl	H	H	H	**5.97**, **6.03**, 7.34, *7.65*, **7.83**, *9.14*, **10.00**, **11.17**, 11.90, **12.17**
5	Me	Me	H	H	**6.02**, 7.27, **7.67**, 8.80, *9.43*. **12.05**, 12.42
6	Cl	Cl	H	H	**5.95**, *7.79*, *8.04*, 9.10, **9.58**, **10.86**, **11.96**
7	Me	H	Me	H	**6.02**, 7.27, *7.46*, **8.05**, *8.71*, 10.01, **11.01**
8	Me	H	*i*-Pr	H	**6.02**, 7.26, *7.39*, *7.68*, 8.06, *8.84*, *9.79*, 9.97, **10.96**
9	*t*-Bu	H	*t*-Bu	H	**6.05**, *7.34*, *7.45*, *8.06*, *8.48*, **9.31**, *9.82*, 10.75, **10.90**, *11.90*, *13.54*
12	Cl	H	Cl	H	**5.95**, *7.66*. **8.36**, **9.80**, **11.18**, 12.59
13	Me	H	H	Me	**6.03**, 7.27, 7.64, *7.80*, *8.51*, 10.71, **10.96**
14	Cl	H	H	Cl	*5.90*, **6.05**, 7.62, **7.83**, **7.89**, **9.64**, **11.03**, **12.70**, *12.80*[d]
15	Me	Me	Me	H	**6.03**,[d] **6.08**, *7.28*, *7.61*, *7.93*, *8.42*, 9.05, **11.33**, 14.83
17	Me	Me	OMe	H	**5.98**, **6.09**, 7.26, *7.36*, *7.53*, *7.89*, **8.14**, 8.48, **9.39**, 11.05, **11.83**, *12.67*
19	Cl	Cl	Cl	H	**5.91**, **5.97**, *7.95*, *8.39*, **9.37**, *11.33*, **12.59**, 14.50
20	Me	Me	Me	Me	**6.09**, *7.29*, *7.67*, 7.94, 9.66, 12.27, 13.19, *14.25*

[a] These cover the range 5–15 μ, except the region 6.10–7.25 μ, where carbon disulfide absorbs strongly. [b] The compounds are numbered in accordance with their type of substitution. [c] Strong bands are given in bold face type, medium intensity bands in italics; very weak bands are not given. [d] Inflection.

TABLE II

SPECTRA OF MINERAL OIL MULLS OF 1,4-BENZOQUINONES[a]

No.[b]	Substituents				Wave lengths of major infrared bands (μ)[c]
	2	3	5	6	
1	H	H	H	H	**6.01**, *6.28*, *7.32*, **7.65**, **9.22**, *9.35*, *10.61*, *11.16*
2	Me	H	H	H	**6.01**, *6.27*, 7.42, *7.70*, 7.80,[d] 8.78, *9.12*, *9.99*, *10.81*, *11.31*, *12.13*, 14.71
5	Me	Me	H	H	**6.02**, *6.24*, 7.32,[d] **7.65**, *8.80*, *9.42*, **12.03**, 12.44
7	Me	H	Me	H	**6.00**, **6.09**, **6.20**, *7.40*, *7.98*, *8.67*, 9.95, *10.80*, *12.57*, 14.11
10	Me	H	OH	H	**6.04**, **6.14**, **6.23**, *7.77*, *8.14*, **8.41**, *11.17*, *12.26*, 13.78
11	Me	H	OMe	H	**5.95**, **6.05**, **6.22**, *7.30*, *8.08*, **8.27**, 8.43, *10.23*, *10.96*, 11.61
13	Me	H	H	Me	**6.05**, *6.20*, *7.60*, *7.76*, 8.30, *8.48*, 9.65, 10.68, **10.87**, 11.08, 12.58
15	Me	Me	Me	H	**6.06**, 6.17, *7.59*, *7.92*, 8.41, 9.04, *11.32*, 14.83
16	Me	Me	OH	H	**6.03**, **6.14**,[d] **6.21**, 7.53, **7.76**, **8.14**, 8.45, 8.66, *9.65*, *11.38*, 12.58, *13.55*
18	Me	OH	Me	H	**6.03**, **6.12**, **6.21**, 6.40, *7.41*, **7.68**, 7.77, *8.36*, *8.89*, *9.47*, 10.40, *11.21*
20	Me	Me	Me	Me	**6.10**, 6.17,[d] *7.65*, *7.95*, 9.73, **14.38**
21	Cl	Cl	Cl	Cl	**5.95**, *6.35*, **9.03**, *9.38*, 11.04, 11.42, *13.30*, **14.06**
22	Br	Br	Br	Br	**5.98**, *6.49*, **8.35**, **9.53**, 11.56, **14.25**

[a] These cover the range 5–15 μ, except the region 6.80–7.30 μ, where mineral oil absorbs strongly. [b] The compounds are numbered in accordance with their type of substitution. [c] Strong bands are given in bold face type, medium intensity bands in italics; very weak bands are not given. [d] Inflection.

to note that in these series, as in another discussed below, the average value of the two bands of compounds with split carbonyl peaks falls satisfactorily into line in the series. As might be anticipated, the most marked effect of the electron-donating substituents examined was found in the case of hydroxyl groups, *i.e.*, compounds 10, 16 and 18 absorb at 6.04 and 6.14, 6.03 and 6.14, and 6.03 and 6.12, respectively. When electronegative groups are introduced the carbonyl band shifts to shorter wave lengths and again the extent of the shift is dependent on the degree of substitution. Thus, the series of chloro compounds 4, 6, 12, 14 and 19 have bands in CS_2 at 5.97 and 6.03, 5.95, 5.95, 5.90 and 6.05, and 5.91 and 5.97 μ, respectively. This correspondence between the nature of the substituents and the positions of the carbonyl bands is clearly associated with the relative ease of release of electrons to the carbonyl groups and is analogous to that observed in the case of simpler conjugated carbonyl systems.[12] The existence of some relationship between the electronegativities of substituents and the position of the carbonyl bands of *p*-benzoquinones has previously been suggested for a limited number of cases by Fuson, Josien and Shelton[6] and by Barchewitz, Tatibouët and Souchay.[7,13]

The bands present in the solid state spectra between 6.17 and 6.28 μ may be assigned to carbon–carbon double bond stretching vibrations by analogy with cyclic αβ-unsaturated ketones.[14] It may be observed that alkyl substitution leads to a shift of this band[15] to lower wave lengths, for in the series of benzoquinone and its methyl derivatives, compounds 1, 2, 5, 7, 13, 15 and 20, the band appears at 6.28, 6.27, 6.24, 6.20, 6.20, 6.17 and 6.17 μ, respectively. This effect is similar to that observed in the case of increased alkyl substitution on

(12) *Cf.*, for example, the effect of substituents on the carbonyl absorption of acetophenone: A. H. Solway and S. L. Friess, THIS JOURNAL, **73**, 5000 (1951); see also ref. 6.

(13) The report of these authors that bromo-, 2,5-dibromo-, tribromo-, 2,5-dimethyl-, 2,5-dimethoxy- and 2,5-dihydroxy-*p*-quinone all absorb "vers 1650 cm.$^{-1}$" (6.06μ) must be treated with some reserve in the light of the present results. Other compounds studied by them, however, are in good agreement with the correlations here discussed.

(14) R. N. Jones, P. Humphries, E. Packard and K. Dobriner, THIS JOURNAL, **72**, 86 (1950).

(15) In all the cases examined only one major band was present in this region.

an isolated double bond[16] and is reminiscent of the report that for several types of α,β-unsaturated ketosteroids the wave length of the C=C stretching vibration decreases as that of the C=O vibration increases.[14] The bands in the hydroxyl containing compounds, 10, 16 and 18, which are situated at 6.23, 6.21 and 6.21 μ, respectively, are at slightly longer wave lengths than those of alkyl compounds with a similar type and degree of substitution and are also considerably increased in intensity, being of comparable strength to the carbonyl bands. The only halogenated compounds examined in the solid state, 21 and 22, have bands at 6.35 and 6.49 μ, respectively, at considerably longer wave lengths than the bands attributed to C=C stretching in the other quinones. Nevertheless, it is considered probable that these bands should also be assigned to this type of vibration in that it is known that substitution of chlorine or bromine on simple ethylenic systems leads to a considerable shift of the C=C stretching band to longer wave lengths. Thus, *cis*-1,2-dichloroethylene and *cis*-1,2-dibromoethylene absorb at 6.29[17] and 6.46 μ,[18] respectively, while propylene absorbs at 6.07 μ.[19,20]

The quinones all exhibit several bands in the 7–10 μ region which are valuable for identification purposes. However, there is no apparent relationship between their position and structural features of the compounds, with the exception of the bands due to symmetrical C–H deformation of the methyl groups of compounds 2, 5, 7, 8, 13, 15, 17 and 20 (CS_2 solution) in the region 7.26–7.31 μ.[21] It is likely that bands arising from in-plane deformation of C–H bonds attached to the quinone nucleus occur in this region, by analogy with similar bands in ethylenic and aromatic systems,[22] but these could not be distinguished.

It was of considerable interest to seek evidence in the region beyond 10 μ of band systems which might be attributable to out-of-plane deformation of hydrogen atoms attached to the quinone nucleus since consistent and fruitful patterns have been established for similar deformation bands in ethylenic[23,24] and benzenoid[25] systems. It was found that the following tentative conclusions could be drawn, applicable to the substituted *p*-benzoquinones examined: (i) *p*-benzoquinones with one or more isolated hydrogen atoms on the ring, *i.e.*, mono-, 2,5-di- and 2,6-disubstituted compounds, have a medium or strong band between 10.9 and 11.4 μ (CS_2 solution)[26,27]; (ii) *p*-benzoquinones with two adjacent hydrogen atoms on the ring, *i.e.*, mono- and 2,3-disubstituted compounds, have a medium or strong band between 11.9 and 12.4 μ (CS_2 solution). These values may be compared with the ranges assigned to out-of-plane deformation of hydrogen atoms on tri- and *cis*-disubstituted ethylenes, *i.e.*, 11.9–12.7 μ[28] and 13.7–14.8 μ,[29] respectively. Although the effect of conjugation on this type of vibration has not been investigated extensively, the evidence available in other cases indicates that the out-of-plane deformation band shifts to lower wave lengths as a result of conjugation,[30] as is here postulated for the case of *p*-benzoquinones. Finally, it is relevant to note that the spectra of a series of Δ^{4}-, $\Delta^{1,4}$- and $\Delta^{4,6}$-3-ketosteroids (all having a trisubstituted C=C in conjugation with the C=O) have in every case a strong band at 11.3–11.6 μ and those of Δ^{1}-, $\Delta^{1,4}$- and $\Delta^{4,6}$-3-ketosteroids (all having a disubstituted C=C in conjugation with the C=O) have a strong or medium band at 12.4–12.9 μ.[31]

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[16] N. Sheppard and D. M. Simpson, *Quart. Rev.* (*London*), **6**, 1 (1952).

[17] T.-Y. Wu, *Phys. Rev.*, **46**, 465 (1934).

[18] G. Emschwiller and J. Lecomte, *J. phys. radium*, **8**, 130 (1937).

[19] E. B. Wilson and A. J. Wells, *J. Chem. Phys.*, **9**, 319 (1941).

[20] Direct comparison with ethylene cannot be made since, due to symmetry, this vibration is inactive in the infrared. The Raman spectrum of ethylene has a band at 6.16 μ which may be used for approximate comparison. Similar trends have been noted in the Raman spectra of halogenated ethylenes: E. Prileshajeva, J. Syrkin and M. Wolkenstein, *Acta Physicochim. U.R.S.S.*, **14**, 119 (1941).

[21] N. Sheppard and D. M. Simpson, *Quart. Rev.* (*London*), **7**, 19 (1953).

[22] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 45, 69.

[23] R. S. Rasmussen, *J. Chem. Phys.*, **15**, 120 (1947).

[24] N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **A196**, 195 (1949).

[25] N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

[26] With the exception of compound 17 which has a weak band in this region.

[27] The range for the solid state spectra is slightly wider: 10.8–11.4 μ.

[28] *Cf.* ref. 22, p. 44.

[29] H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

[30] W. Oroshnik and D. Mebane, This Journal, **76**, 5719 (1954).

[31] R. N. Jones, F. Herling and E. Katzenellenbogen, *ibid.*, **77**, 651 (1955).