discussion it was assumed that all intramolecular energy transfer occurs by radiationless resonance mechanism.[5] The absorption spectra of the molecules studied represent superpositions of anthracene and naphthalene spectra, and this fact proves that there is no overlap between the two π-electron systems. No energy transfer is, therefore, expected by way of the hydrocarbon chain.

Acknowledgment.—The authors are indebted to Miss Z. Silberman for her assistance in this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LAVAL UNIVERSITY, QUEBEC, CANADA]

Infrared Spectra of Some Substituted *p*-Benzoquinones

BY JEHANBUX F. BAGLI[1]

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The infrared spectra of a number of halogenated *p*-benzoquinones are examined between 1800–800 cm.$^{-1}$. The influence of an α-halogen atom on the perturbation of the carbonyl stretching mode is discussed. The out-of-plane deformation of the hydrogen atoms attached to a substituted *p*-benzoquinone nucleus observed by earlier workers is confirmed and extended over a wider range of compounds. An attempt is made to characterize frequencies in the 1400–1000 cm.$^{-1}$ region of the spectra and to deduce a relationship between the characteristic bands and the structure of the isomeric disubstituted (2,3, 2,5 and 2,6) *p*-benzoquinones having one or both substituents as halogen atoms.

The study of the infrared spectra of substituted *p*-benzoquinones represents only a small portion of the spectroscopic studies of quinones. Most of these studies[2] were directed only towards the examination of the carbonyl stretching mode of the quinone molecule. More recently, two publications[3,4] have appeared wherein all the major bands in the infrared spectra of the substituted *p*-benzoquinones are mentioned. Whereas the study of the German group[4] is restricted to the alkyl, hydroxy and methoxy substituted *p*-benzoquinones, that of the American workers[3] includes a few halogenated derivatives.

Over the last few years, several aryl- and haloaryl-*p*-benzoquinones have been synthesized[5,6] in this Laboratory. We have examined the spectra of some of these compounds, and in the present paper report some correlations that result from the investigation.

Results and Discussion

C=O Stretching Frequencies.—The carbonyl stretching frequencies of the *p*-benzoquinones examined are listed in Table I. The data shows that of the twenty eight compounds listed, ten exhibit a doublet in the carbonyl region. Some evidence has already been put forth[7] on the nature of the splitting of the C=O band of *p*-benzoquinone (no. 1).

Splitting of the bands in the carbonyl region of an infrared spectrum of a compound possessing two C=O groups can be caused by (1) vibrational coupling between suitably located vibrations of the same frequency within a molecule, as that demonstrated for diacyl peroxides and anhydrides,[8] (2) intramolecular vibrational effect of the type recently reported by Jones and co-workers[9] or (3) separation of the unperturbed frequencies of the stretching mode of two carbonyls caused by steric, electronic or electrical influences prevailing in a molecule. These factors may operate singly or jointly to influence the C=O stretching vibrations. Thus with increased separation of the unperturbed frequencies, the vibrational coupling would be expected to diminish. It has been suggested[7] that the two carbonyl bands in chloro-*p*-benzoquinone (no. 2) do not result from an intramolecular vibrational effect of the type postulated for *p*-benzoquinone. That the two bands in the carbonyl region of benzoquinones No. 2, 5, 6, 11 and 12 are indeed caused by the separation of the unperturbed vibrations of the two carbonyls is readily seen from an analysis of the data in Table I.

Introduction of a chlorine atom in *p*-benzoquinone produces two carbonyl bands (Fig. 1), the relative intensities of which are independent of the polarity of solvent.[7] The $\Delta\nu$ value between these bands is 20 cm.$^{-1}$. This value is in excellent agreement with those recorded for a positive shift of the carbonyl band due to the dipolar field effect in α-halo (equatorial)-cyclohexanone[10] and in α-halo-α,β-unsaturated ketones.[11] Thus the band at 1680 cm.$^{-1}$ (Band A) in no. 2 may be assigned to the carbonyl group with the halogen atom α to it, whereas the one at 1660 cm.$^{-1}$ (Band B) is attributable to the carbonyl flanked by two hydrogens. The following facts strongly support the above postulate. The introduction of another chlorine atom α to the second carbonyl as in nos. 3 and 4 produces a single intense band at 1692 and 1686 cm.$^{-1}$, respectively (Fig. 1). On the other

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[1] National Research Council of Canada Postdoctoral Fellow 1959–1960. Present address, Ayerst, McKenna & Harrison, P. O. Box 6115, Montreal, P.Q.

[2] For references to these studies see ref. 3.

[3] P. Yates, M. I. Aradao and L. F. Fieser, *J. Am. Chem. Soc.*, **78**, 650 (1956).

[4] von W. Flaig and J. C. Salfeld, *Ann.*, **626**, 215 (1959).

[5] P. Brassard and P. L'Ecuyer, *Can. J. Chem.*, **36**, 700 (1958).

[6] (a) P. Brassard and P. L'Ecuyer, *ibid.*, **36**, 814 (1958); (b) J. F. Bagli and P. L'Ecuyer, *ibid.*, **38**, 1037 (1961).

[7] J. F. Bagli, *J. Phys. Chem.*, **65**, 1052 (1961).

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

[9] R. N. Jones, C. L. Angell, T. Ito and R. J. D. Smith, *Can. J. Chem.*, **37**, 2007 (1959).

[10] (a) E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **77**, 5418 (1955); (b) R. N. Jones, P. Humphries and K. Dobriner, *ibid.*, **72**, 956 (1950).

[11] (a) R. N. Jones, D. A. Ramsey, F. Herling and K. Dobriner, *ibid.*, **74**, 2828 (1952); (b) G. R. Allen and N. J. Weiss, *ibid.*, **82**, 2840 (1960).

TABLE I

CARBONYL STRETCHING FREQUENCY OF *p*-BENZOQUINONES IN $CHCl_3$

No.	Substituent 2	3	5	6	Frequency, cm.$^{-1}$ Band A	Band B	$\Delta\nu$, cm.$^{-1}$ Band A–B	Ref
1	H	H	H	H	1674	1662		[d]
2	Cl	H	H	H	1680	1660	20	[e]
3	Cl	Cl	H	H	1692			[e]
4	Cl	H	Cl	H	1686			[d]
5	Cl	H	H	Cl	1702	1661	41	[d]
6	Cl	Cl	Cl	H	1692	1675	17	[a]
7	Cl	Cl	Cl	Cl	1693			[d,b]
8	Br	H	H	H	1682			[f]
9	Br	Br	H	H	1681			[e]
10	Br	H	Br	H	1678			[e]
11	Br	H	H	Br	1703	1663	40	[f]
12	Br	Br	Br	H	1696	1674	22	[e]
13	Br	Br	Br	Br	1672			[a]
14	Ph	H	H	H	1671	1663[c]		[e]
15	Cl	Ph	H	H	1683			[e]
16	Cl	H	Ph	H	1674			[e]
17	Cl	H	H	Ph	1688	1659	29	[e]
18	*p*-NO_2Ph	H	H	H	1670			[e]
19	Cl	*p*-NO_2Ph	H	H	1686			[e]
20	Cl	H	*p*-NO_2Ph	H	1679			[e]
21	Cl	H	H	*p*-NO_2Ph	1682	1657	25	[e,b]
22	*p*-Cl-Ph	H	H	H	1664			[e]
23	Cl	*p*-Cl-Ph	H	H	1679			[e]
24	Cl	H	*p*-Cl-Ph	H	1674			[e]
25	Cl	H	H	*p*-Cl-Ph	1685	1658	27	[e]
26	Cl	Cl	*p*-NO_2Ph	H	1688			[e]
27	Cl	*p*-NO_2Ph	Cl	H	1686			[e]
28	Cl	*p*-NO_2Ph	H	Cl	1698	1663	35	[e]

[a] Values quoted from ref. 3 (no. 6 in CS_2 and no. 13 in KBr). [b] Saturated solution used. [c] Inflection. [d] Purified sample of commercial material. [e] Synthesized in this Laboratory (ref. 5 and 6). [f] Prepared, see Experimental.

hand, the presence of a second chlorine atom in position 6, as in no. 5, produces two carbonyl bands 41 cm.$^{-1}$ apart. This separation is exactly double that observed for monochloro-*p*-benzoquinone. Trichloro-*p*-benzoquinone[12] (no. 6) presents an interesting case. It exhibits two bands in the carbonyl region 17 cm.$^{-1}$ apart. It is noteworthy that the low frequency band (1675 cm.$^{-1}$) attributable to the carbonyl flanked by a hydrogen and a chlorine atom is significantly shifted ($+\Delta\nu$ 15 cm.$^{-1}$) to the higher frequency, lending further support to our contention. Lastly, chloranil (no. 7) as expected shows a single[13] intense carbonyl band at 1693 cm^{-1}.

The single carbonyl band exhibited by bromo-*p*-benzoquinones (nos. 9, 10 and 13) and doublets observed in the case of 2,6-dibromo-*p*-benzoquinone (no. 11) and tribromo-*p*-benzoquinone (no. 12) are also readily explicable based on the above rationale. The monobromo-*p*-benzoquinone however, presents the only exception.[14]

The introduction of an aryl group in *p*-benzoquinone has little or no influence on the carbonyl vibrations. This is readily discerned from the bands listed for compounds nos. 14, 18 and 22. The presence of a chlorine atom in the aryl-*p*-benzoquinones examined produces an influence on the carbonyl band which is dependent upon the relative positions of the chlorine atom and the aryl group. Thus when the two groups are located α to the two different carbonyls of *p*-benzoquinone (nos. 15, 16, 19, 20, 23 and 24), the compound exhibits a single carbonyl band. In contrast, when the chlorine and the phenyl groups flank the same carbonyl (nos. 17, 21 and 25), a doublet is observed in the carbonyl region.

Jones and co-workers[15] have pointed out that a *para* substituent on the phenyl β to the carbonyl in tetracyclones produces a small negative shift (0 to -8 cm.$^{-1}$) in the position of the carbonyl band, indicating a weak conjugation effect.

If the above observation is extended to the com-

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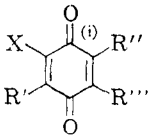
(12) See footnote (a) Table I.

(13) Although the concept of dipolar field effect satisfactorily explains the carbonyl doublet, in the spectra of halogenated-*p*-benzoquinones, it must not be overlooked that in molecules not possessing D_{2h} symmetry both antisymmetric and symmetric vibrations of carbonyl group will be active in the infrared and will contribute to the carbonyl absorption. (P. Souchay, Tatibouet and P. Barchewitz, *J. Phys. Radium*, **15**, 533 (1954)). In contrast in molecules such as chloranil (no. 7) and bromanil (no. 13), failure to show two bands may result from the symmetrical vibrations being totally forbidden in the infrared. (M. L. Josien, N. Fuson, J. M. Lebas and J. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953)).

(14) It is well established that the field effect due to halogen atom decreases in the order Cl > Br > I. It is not improbable, that in the case of bromo-*p*-benzoquinone the stretching frequencies of the two carbonyls lie too close to be resolved under the experimental conditions used.

(15) R. N. Jones, C. Sandorfy and D. E. Trucker, *J. Phys. Radium*, **15**, 320 (1954).

pounds under consideration, the variation in the carbonyl band becomes readily explicable. In Ia and Ib the carbonyl group (i) is simultaneously under the influence of two opposing effects, *viz.* the field effect due to the halogen atom, causing a positive shift, and the conjugation due to the β-phenyl group causing a negative shift. The resultant influence of these two forces should be to reduce the separation of the unperturbed frequencies of the two carbonyls. This may cause the carbonyl bands to overlap to an extent that prevents resolution of the individual peaks. Conversly, in the case Ic these two effects are associated with two different carbonyls, enhancing the separation of two bands. That this indeed is the case is demonstrated in Table I. The $\Delta\nu$ values between the two carbonyl peaks of compounds Nos. 17, 21 and 25 are significantly higher than that observed for chloro-p-benzoquinone. Finally, the $\Delta\nu$ value between the two carbonyl bands of 2,6-dichloro-p-nitrophenyl-p-benzoquinone (no. 27) of 35 cm.$^{-1}$ is also readily explicable, based on the above argument.

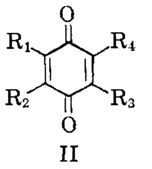


I

(a) R′ = phenyl, R″ = R‴ = H, X = Cl
(b) R′ = R″ = H, R‴ = phenyl, X = Cl
(c) R′ = R‴ = H, R″ = phenyl, X = Cl

It should be noted that the carbonyl bands of 2,5-disubstituted halo-aryl-p-benzoquinones (nos. 16, 20 and 24) are located 5–9 cm.$^{-1}$ lower than those observed for 2,3-disubstituted isomers (nos. 15, 19 and 23). This may serve as helpful supporting evidence in deciding the structure of these isomers.

Out-of-plane C–H Deformation.—Yates and coworkers[3] were the first to make tentative assignments to the bands attributable to C–H out-of-plane deformation of the hydrogens attached to p-benzoquinone. The C–H bending frequencies of the compounds examined are listed in Table II. It is noted that all monosubstituted p-benzoquinones, of the type IIa, exhibit two bands of medium intensity (one between 865–825 cm.$^{-1}$ and the other between 916–901 cm.$^{-1}$), as against one band (between 920–840 cm.$^{-1}$) observed



II

(a) $R_1 = R_2 = R_3 = H$
(b) $R_1 = R_2 = H$
(c) $R_1 = R_3 = H$
(d) $R_1 = R_4 = H$

for all disubstituted compounds. It has been noted in the case of isomeric disubstituted aromatic compounds that the energy of C-H bending vibrations generally increases with the separation of free hydrogens.[16] In 2,3-disubstituted p-benzoquinone (IIb) with two vicinal hydrogen atoms, the C–H bending band occurs between 846–841 cm.$^{-1}$. On the other hand, the C–H deformation of hydrogens separated by one or two carbon atoms, as in 2,5- and 2,6-disubstituted p-benzoquinones (IIc and IId, respectively) occurs between 920–897 cm.$^{-1}$. In the light of the above observation, it seems reasonable to assign the high frequency band of monosubstituted p-benzoquinone to the C-H bending of the isolated hydrogen and the low frequency band[17] to the two vicinal hydrogens. It may be mentioned that C–H deformation bands of all 2,5-disubstituted isomers studied are found 6–10 cm.$^{-1}$ removed towards lower frequency relative to those of the corresponding 2,6-isomers.

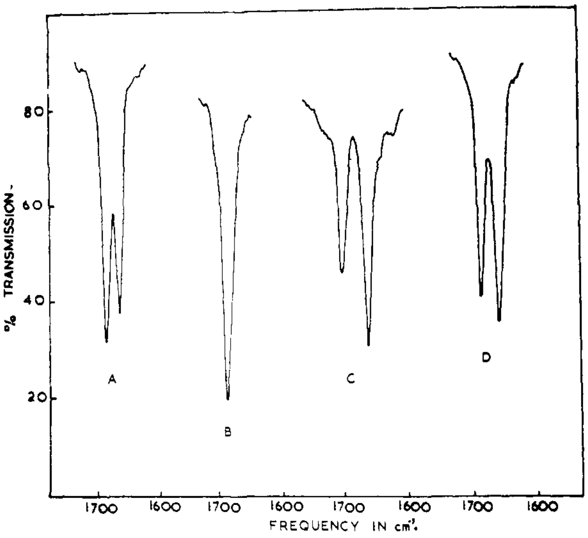


Fig. 1.—Infrared spectrum in C=O stretching region in $CHCl_3$: A, chloro-p-benzoquinone (no. 2); B, 2,5-dichloro-p-benzoquinone (no. 4); C, 2,6-dichloro-p-benzoquinone (no. 5); D, 2-chloro-6-phenyl-p-benzoquinone (no. 17).

Other Major Bands Between 1300–1000 Cm.$^{-1}$.—It has been shown in the steroid series that ketonic function is associated with characteristic absorption[18] below 1350 cm.$^{-1}$. In our studies with p-benzoquinones we have noted similar absorption in the 1300–1000 cm.$^{-1}$ region. These bands are listed[19] in Table II. It is observed that 2,3-disubstituted compounds are characterized by a medium or strong intensity band around 1104–1090 cm.$^{-1}$, accompanied by a pair of medium in-

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[16] R. N. Jones and C. Sandorfy, "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 391.

[17] The C–H deformations of the hydrogens attached to p-benzoquinones nos. 14, 15, 16 and 17 are separated to such an extent as not to be perturbed by analogous vibrational modes of hydrogens on the phenyl ring (740–700 cm.$^{-1}$). However, it must be noted that the low frequency C–H deformations in compounds no. 18, 19 and 22, 23 are subject to perturbation by the C–H bending mode of the hydrogens on 1,4-disubstituted phenyl ring.

[18] R. N. Jones, F. Herling and E. Katzenellenbogen, *J. Am. Chem. Soc.*, **77**, 651 (1955).

[19] It may be mentioned that aryl-p-benzoquinones showed other characteristic bands, ascribable to in-plane deformations of aryl hydrogens. However, those listed in Table II are the ones common to both non-aryl and aryl p-benzoquinones.

TABLE II

MAJOR ABSORPTION BANDS BETWEEN 1350–800 CM.$^{-1}$

No.	Out-of-plane C-H deformation			Other major bands			
				Monosubstituted *p*-benzoquinones			
2	901	825		1312	1280	1095	1002
8	904	821		1309	1277	1095	975
14	910	836		1298	1278	1095	977
18	916	865	858[a]	1295	1275	1092	979
22	913	850		1302	1285	1086	977
				2,3-Disubstituted *p*-benzoquinones			
3	841			1290	1256	1104	1050
9	836			1270	1235	1092	1012
15	844			1303	1269	1099	1019
19	853[a]	844		1306	1268	1098	1016
23	846			1301	1274	1095	1017
				2,5-Disubstituted *p*-benzoquinones			
4	897			1310	1225–1205[b]		1025
10	900			1310	1222–1200[b]	1187	995
16	910			1321	1225–1208[b]	1182	1019
20	913	856[a]		1320	1225–1202[b]	1182	1015
24	912			1320	1227–1203[b]	1183	1017
				2,6-Disubstituted *p*-benzoquinones			
5	907			1281	1041		
11	911			1272	1007		
17	919			1297	1013		
21	919	853[a]		1288	1010		
25	918			1295	1012		

[a] These bands are attributable to C–N stretching vibrations of aromatic nitro- group (*cf.* R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952)) [b] The broadness of these bands seems to be associated with the absorption of solvent ($CHCl_3$) in this region. The spectra in CS_2 showed a sharp, well defined peak in this region.

tensity bands (1310–1270 and 1275–1235 cm.$^{-1}$. In 2,5-disubstituted isomers a similar pair occurs at 1227–1200 and 1187–1183 cm.$^{-1}$ accompanied by a weak band between 1320–1310 cm.$^{-1}$. On the other hand, the 2,6-isomers exhibit only a single medium or strong intensity band between 1297–1272 cm.$^{-1}$. It is impossible at the present time to assign these bands to any particular mode of molecular vibrations. However, their usefulness in arriving at the structure of isomeric, disubstituted *p*-benzoquinones cannot be overlooked.

Experimental

The spectra were all recorded in solution (0.1 *M*), on a Beckman IR-4 spectrophotometer equipped with a NaCl prism. The chloroform[20] and carbon disulfide used were ANALAR grade (B.D.H.) and reagent grade (Merck), respectively. The spectra were calibrated by the use of a polystyrene film. The sources of the *p*-benzoquinones studied are listed in the footnotes to Table I.

Bromo-*p*-benzoquinone.—This was obtained by duplicating the procedure described,[21] m.p. 56–57°: ν $CHCl_3$ 904,821 (C-H deformation), 1682 ($>$C=O stretching) cm.$^{-1}$.

2,6-Dibromo-*p*-benzoquinone.—This material was synthesized as described,[22] m.p. 132–133°, reported 130–131°. ν $CHCl_3$ 911 (C-H deformation), 1663, 1703 ($>$C=O stretching) cm.$^{-1}$. λmax 290 mμ (log ϵ 4.18), 352 mμ (log ϵ 2.92); reported[23] λmax 291 mμ (log ϵ 4.11), 352 mμ (log ϵ 2.90).

Acknowledgments.—The author wishes to thank Dr. Ph. L'Ecuyer for his encouragment during this work. Reading of the manuscript by Professor R. N. Jones is gratefully acknowledged.

(20) Although chloroform is used as a solvent of choice, in order to eliminate the hydrogen bonding as a possible source of frequency shift; wherever possible, (solubility permitting) the spectra of compounds exhibiting a doublet in the $>$C=O region are also recorded in carbon disulfide. Thus the carbonyl region of compounds No. 2, 5, 11, 17 and 25 in carbon disulfide also exhibit a doublet. The $\Delta\nu$ value between these two bands are found to be essentially identical with those observed when chloroform was used.

(21) von E. Sarauw, *Ann.*, **209**, 93 (1881).

(22) van Erp, *Rec. trav. chim.*, **30**, 284 (1911).

(23) E. A. Braude, *J. Chem. Soc.*, 490 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE, NEWARK, DELAWARE]

The Reaction of Decaborane with Amines and Related Compounds[1]

BY HAROLD C. BEACHELL AND DONALD E. HOFFMAN

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Strongly basic aliphatic amines form salt-type adducts with decaborane without the evolution of hydrogen. The treatment of decaborane with *sym*-diethylthiourea, a poor electron donor, results in the formation of $B_{10}H_{12}[(C_2H_5NH)_2CS]_2$ with the stoichiometric evolution of hydrogen. A two-step mechanism is proposed for this second order reaction. Nitrogen heterocycles do not participate in completely defined reactions with decaborane.

The reactivity of decaborane ($B_{10}H_{14}$) with nitrogen compounds appears to be quite dependent on the electron donor ability of the nitrogen substrate and experimental conditions. Fetter and Burkardt[2] report that decaborane and pyridine react at 0° in the absence of solvents to form $B_{10}H_{14}(C_5H_5N)_2$ without the evolution of hydrogen. In benzene and at higher temperatures, however, the reaction evolves hydrogen in amounts which are inversely proportional to the pyridine:decaborane ratio.

Similar dependence on reaction conditions was reported for the treatment of decaborane with a strong electron donor such as dimethylamine, resulting in the formation of adducts which may contain 1–3 moles of amine per mole of boron hydride.[3] No hydrogen evolution was reported for this particular reaction. Diethylcyanamide,

(1) Taken in part from the dissertation submitted by Donald E Hoffman to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1960.

(2) N. R. Fetter and L. A. Burkardt, Abstracts of Papers, 135th National Meeting, Am. Chem. Soc., Boston, Mass., 1959, p. 45 M.

(3) S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **80**, 5911 (1958).