

## PREPARATION AND INFRARED SPECTRA OF ANTHRAQUINONE AND ITS METHYL DERIVATIVES AND OF QUINONES RELATED TO POLYNUCLEAR AROMATIC HYDROCARBONS

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The infrared spectra were measured of solid samples of anthraquinone, its 1-, 2-methyl-, 1,2-, 1,3-, 1,4-, 2,3-, 2,6-, 2,7-dimethyl-, 2,3,6-trimethyl- and 2,3,6,7-tetramethyl derivatives, as well as of naphthacene-6,11-quinone and its 1,2,3,4-tetrahydro derivative, pentacene-6,13-quinone and pentacene-5,7,12,14-diquinone. Absorption bands belonging to the characteristic vibrations of quinoid arrangement, aromatic rings and their hydrogen atoms, and methyl group were found.

In spite of the fact that quinones of polynuclear aromatic hydrocarbons belong to easily obtainable, compounds, their infrared spectra have not yet been studied systematically. A considerable complexity of these spectra resulting in difficulties during the identification of individual bands is evidently one of the reasons. Nevertheless, some authors studied some dependences in spectra of quinones<sup>1-6</sup>, especially a very strong band related to the vibration of the CO group of quinoid structure. Thus, Josien with coworkers<sup>1</sup> investigated the change of the CO vibration frequency in dependence on the cycle number of the linearly condensed polycyclic quinones, further, the effect of electrophilic and nucleophilic substituents on the frequency of the same band<sup>2</sup> and the effect of polar substituents on the ring stretching bands of polynuclear quinones<sup>2</sup> were examined.

In the present paper, we reproduce the spectra of anthraquinone, 1- and 2-methylanthraquinones, 1,2-, 1,3-, 1,4-, 2,3-, 2,6-, and 2,7-dimethylanthraquinones, 2,3,6-trimethylanthraquinone, 2,3,6,7-tetramethylanthraquinone, naphthacene-6,11-quinone- and its 1,2,3,4-tetrahydro derivative, pentacene-6,11-quinone- and pentacene-5,7,12,14-diquinone, the characteristics of which are given in Table I.

The anthraquinones and naphthacenequinones studied are easily obtainable either by acid catalyzed cyclization<sup>7-13</sup> of products of the Friedel-Crafts reaction of phthalic anhydride with aromatic hydrocarbons<sup>11-17</sup> or of products of the Grignard synthesis<sup>7,18,19</sup>, or by the Diels-Alder addition of linear dienes to *p*-benzoquinone<sup>20,21</sup> or methylated naphtho-1,4-quinone<sup>22</sup> followed by dehydrogenation of the adducts formed<sup>22</sup>. Preparation methods for quinones derived from pentacene were also described and studied<sup>23-25</sup>. Monoquinone<sup>23,24</sup> is formed easily by a base-catalyzed condensation of phthalic aldehyde with cyclohexane-1,4-dione and diquinone is produced by cyclization of the Friedel-Crafts product of benzene-1,2,4,5-tetracarboxylic acid dianhydride (pyromellitic dianhydride) with benzene<sup>25</sup>.

TABLE I  
Characteristics of Polynuclear Quinones

Compound and its preparation <sup>a</sup>	Solvent <sup>b</sup>	M.p., °C (ref.)
Anthraquinone (I), A	CH <sub>3</sub> COOH	286/285—286 (33)
1-Methylanthraquinone (II), B	CH <sub>3</sub> COOH	174/171—173 (7)
2-Methylanthraquinone (III), A	CH <sub>3</sub> COOH	176/173 (8)
1,2-Dimethylanthraquinone (IV), B	CH <sub>3</sub> COOH	154/154—155 (19)
1,3-Dimethylanthraquinone (V), A	CH <sub>3</sub> COOH	162/162 (9)
1,4-Dimethylanthraquinone (VI), A	CH <sub>3</sub> COOH	142/141 (10)
2,3-Dimethylanthraquinone (VII), A	CH <sub>3</sub> COOH	210/208 (11)
2,6-Dimethylanthraquinone (VIII), C	C <sub>2</sub> H <sub>5</sub> OH	242/242 <sup>d</sup> (34)
2,7-Dimethylanthraquinone (IX), C	C <sub>2</sub> H <sub>5</sub> OH	169/170 <sup>d</sup> (34)
2,3,6-Trimethylanthraquinone (X), C	CH <sub>3</sub> COOH	239/240 <sup>d</sup> (35)
2,3,6,7-Tetramethylanthraquinone (XI), C	CH <sub>3</sub> COOH	331/330 (21)
Naphthacene-6,11-quinone (XII), A	TCE	293/294 (26)
1,2,3,4-Tetrahydronaphthacene-6,11-quinone (XIII), A	CH <sub>3</sub> COOH	211/211 (13)
Pentacene-6,13-quinone (XIV), D	DMF	378/378 (23, 24)
Pentacene-5,7,12,14-diquinone (XV), A	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	412/408 (25)

<sup>a</sup> The number in parentheses gives the method of preparation used for individual quinones (see Experimental); <sup>b</sup> the solvent used for crystallization, TCE 1,1,2,2-tetrachloroethane, DMF dimethylformamide, <sup>c</sup> the former value belongs to the compound studied in this work (from the Koffler block without any correction), the latter is taken from literature (with corresponding references in parentheses); <sup>d</sup> values from the literature with a correction.

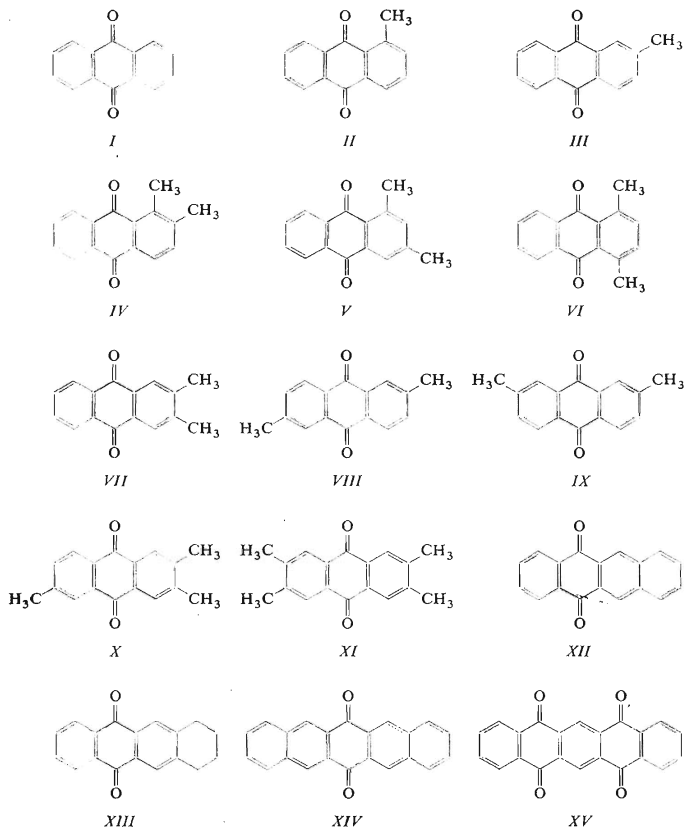
The wavenumbers of absorption bands of these quinones in the range studied are collected in Table II, where some bands also are tentatively interpreted.

## EXPERIMENTAL

### Preparation Methods for Quinones

A) *Friedel-Crafts synthesis and cyclization*<sup>8-17</sup>. To the mixture of 14.8 g (0.1 mol) finely ground phthalic anhydride and 0.11 mol aromatic hydrocarbon in 15 ml symmetric tetrachloroethane, 30 g anhydrous AlCl<sub>3</sub> was added slowly with stirring. After a vigorous reaction subsided, during which the reaction mixture was heated to 50–60°C, the mixture was stirred for 1 hour at room temperature. Then, the reaction mixture was introduced into 300 ml mixture of ice and water acidified with 30 ml 37% HCl, water was separated from the oily product which was then washed with water several times. The solvent and excess hydrocarbon were steam stripped and the solid raw product was purified by precipitation from alkaline solution with diluted HCl. In such manner the substituted 2-benzoylbenzoic acids, which were used for cyclization without further purification, were obtained in high yields.

Cyclizations were carried out by heating the solution of keto acid in concentrated H<sub>2</sub>SO<sub>4</sub> for 60 min at 115–130°C (with the exception of anthraquinone, 2,3-dimethylanthraquinone, and 1,2,3,4-tetrahydronaphthacenequinone preparations, for which the heating times were 30, 20,



and 15 min, resp.). The H<sub>2</sub>SO<sub>4</sub> keto acid molar ratio was chosen 20–25. The resulting quinones were isolated by careful pouring the chilled reaction mixture into the mixture of ice and water. The precipitate formed was filtered, washed with water, 5% aqueous Na<sub>2</sub>CO<sub>3</sub> solution, with water again, and finally dried in air. Raw products so obtained were purified by crystallization from acetic acid (activated carbon) and yielded pure quinones in good yields (68–92%), with the exception of 1,2,3,4-tetrahydronaphthacene-6,11-quinone which was isolated in an essentially

lower yield, in comparison with literature data<sup>13</sup>. Probable reason is the use of concentrated  $H_2SO_4$  instead of 25% oleum, as recommended in literature, for performing the cyclization. We also failed in obtaining the by-product of this cyclization, 1,2,3,4-tetrahydro-1,2-benzanthraquinone, by crystallization from benzene or acetic acid<sup>13</sup>. On the other hand, we prepared in a small amount an analogous by-product of the *o*-xylylbenzoic acid cyclization, 1,2-dimethylanthraquinone, using the separation by crystallization from acetic acid and acetone<sup>11</sup>, recommended in literature.

By using naphthalene-2,3-dicarboxylic acid anhydride as a component of the Friedel-Crafts reaction with benzene in symmetric tetrachloroethane, the corresponding keto acid<sup>26</sup> was prepared in a good yield. By its cyclization in concentrated  $H_2SO_4$  at 130°C, naphthalene-6,11-quinone occurred in an essentially lower yield as compared with literature data for the cyclization in the melt of aluminium and sodium chlorides<sup>26</sup>.

Similarly, pentacene-5,7,12,14-tetrone (pentacene-5,7,12,14-diquinone)<sup>25</sup> was prepared in a high yield by the Friedel-Crafts reaction of benzene-1,2,4,5-tetracarboxylic acid dianhydride (pyromellitic dianhydride) with benzene in symmetric tetrachloroethane and by following cyclization of intermediate product in concentrated  $H_2SO_4$  at 100°C. The characteristics of quinones are given in Table I.

B) *Grignard synthesis*<sup>7,18,19</sup>. The solution of Grignard reagent was prepared from 0.035 mol arylbromide and 850 mg (0.035 mol) magnesium shavings in 13 ml dry diethyl ether. The reaction was initiated by several drops of methyl iodide and completed by 3-hour boiling under reflux. Phthalic anhydride (4.65 g, 0.031 mol) was stirred up in 45 ml dry benzene and heated to boil with stirring. Into this suspension, the Grignard reagent solution was dropped during 20 min and the mixture was then refluxed for 2 hours with stirring. After cooling to laboratory temperature, the suspension was introduced into water acidified with HCl and the mixture occurring was steam distilled. The raw product, remaining in the boiling flask, was washed with water, dissolved in 4% aqueous NaOH solution and precipitated by acidifying with HCl. Before the cyclization to quinone, the keto acid was purified by crystallization. The yields of pure keto acids were round 80%. Cyclizations were performed in the same way as in the preceding paragraph. The characteristics of resulting quinones are also given in Table I.

C) *Diene synthesis*. 6-Methyl-1,4-naphthoquinone and 6,7-dimethyl-1,4-naphthoquinone were prepared by the addition of isoprene<sup>27</sup>, or 2,3-dimethyl-1,3-butadiene to *p*-benzoquinone<sup>28</sup> and by the oxidation of the addition product with  $CrO_3$  in acetic acid according to the method described<sup>27</sup>.

The additions of isoprene and 2,3-dimethyl-1,3-butadiene to naphtho-1,4-quinones were carried out by refluxing the solution of both reaction components the diene to naphthoquinone molar ratio was 2 : 1) in ethyl alcohol for 5 hours<sup>27</sup>. Addition products (1,4,4a,9a-tetrahydroanthraquinones), which were obtained in good yields (85–90%), were dehydrogenated to corresponding anthraquinones after crystallization and possible separation of position isomers<sup>29</sup>.

Dehydrogenations were performed by introducing moderate oxygen flow into the tetrahydroanthraquinone<sup>22</sup> solution in diluted (5%) alcoholic KOH solution for 150 min at moderately increased temperature. Thus, 2,6- and 2,7-dimethylanthraquinones<sup>29</sup> from isoprene and 6-methyl-1,4-naphthoquinone as well as 2,3,6-trimethyl- and 2,3,6,7-tetramethylanthraquinone from isoprene or 2,3-dimethyl-1,3-butadiene and 6,7-dimethyl-1,4-naphthoquinone<sup>29</sup> were obtained in good yields.

D) *Pentacene-6,13-quinone* was prepared by the condensation of phthalic aldehyde with 1,4-cyclohexanedione in ethyl alcohol at ordinary temperature according to the described method<sup>23,24</sup> and purified by sublimation *in vacuo* in the  $CO_2$  flow.

TABLE II  
Vibrational Assignment of Quinones I–XV

Vibrational assignment	I	II	III	IV	V	VI
	3 326 w	3 326 w	3 319 w	3 320 w	3 320 w	3 315 w
	3 304 sh	—	—	—	—	—
	3 260 vw	3 255 vw	—	3 250 vw	3 255 vw	3 257 vw
	—	3 175 vw	—	3 150 sh	—	—
	—	—	—	—	—	—
Region of CH-stretching bands-arom.	—	—	—	3 105 m	—	3 093 m
	3 078 w	3 080 sh	3 075 w	3 075 m	3 072 m	3 074 m
	3 050 vw	3 068 w	3 045 w	3 052 m	3 052 sh	3 055 w
	—	3 045 sh	—	—	—	3 040 w
	3 010 vw	3 012 vw	3 010 sh	3 012 w	3 020 sh	—
	—	—	—	—	—	3 017 m
CH-stretching bands aliphatic, resp. some arom.		2 975 m	2 980 sh	2 980 m	2 986 m	2 981 s
		—	—	2 962 w	2 975 sh	2 971 m
		—	2 950 sh	—	—	—
CH <sub>2</sub> asym. and CH <sub>2</sub> aromat. CH stretch. arom.	—	—	—	—	—	—
	2 932 w	2 932 m	2 929 m	2 935 w	2 930 m	2 929 s
	—	2 900 sh	—	2 908 sh	2 900 sh	2 900 sh
	—	—	—	2 875 sh	—	—
CH <sub>3</sub> sym. and CH arom. CH <sub>2</sub> sym. and arom. b.	2 858 w	2 862 w	2 863 w	—	2 858 w	2 863 w
	—	—	—	—	—	—
	—	—	—	—	—	—
	2 763 vw	2 740 vw	2 735 sh	2 750 vw	2 745 vw	2 745 vw
	—	—	—	—	—	—
	—	—	2 700 sh	—	2 720 sh	—
	2 680 sh	—	2 660 vw	2 665 vw	2 683 sh	—
	—	—	—	—	—	—
	2 658 w	2 650 vw	2 640 sh	—	2 655 vw	2 650 vw
	2 630 vw	—	—	—	—	—
	—	—	—	—	2 602 vw	—
	—	—	—	—	—	—
	2 485 vw	2 440 vw	—	—	—	—
	2 410 vw	—	—	—	—	—
	—	—	—	—	—	—
	2 370 vw	—	—	2 365 w	2 373 vw	—
	—	—	—	—	—	2 290 vw
	2 255 vw	2 270 vw	2 240 vw	—	—	—
	—	—	—	—	—	—

TABLE II  
(Continued)

VII	VIII	IX	X	XI	XII	XIII	XIV	XV
3 320 w	3 318 w	3 325 w	3 320 w	3 320 w	3 325 w	3 332 w	3 318 w	3 331 w
—	—	—	—	—	—	3 310 sh	—	3 272 sh
3 250 sh	3 250 vw	3 260 sh	—	—	3 240 sh	3 250 sh	3 238 vw	3 250 vw
—	3 206 vw	3 200 sh	3 201 vw	3 198 vw	3 205 sh	3 190 vw	3 203 vw	3 179 vw
—	—	—	—	3 160 vw	—	—	—	—
—	3 103 sh	3 105 sh	3 105 sh	—	—	3 096 sh	—	3 102 m
3 072 sh	—	—	—	—	3 070 m	3 070 m	3 080 sh	—
3 068 w	3 055 m	3 065 w	3 058 m	3 054 m	3 052 sh	3 050 w	3 055 s	3 069 m
3 055 w	3 040 m	—	—	—	—	—	—	3 043 m
3 035 sh	—	3 030 w	3 028 w	3 035 sh	—	3 028 sh	3 030 sh	3 012 w
3 010 vw	—	—	—	—	—	3 012 sh	3 000 sh	—
2 985 m	—	2 980 sh	2 990 s	2 984 m	—	—	—	—
—	—	—	2 975 m	—	—	—	—	—
2 955 m	2 958 w	2 955 sh	2 955 m	2 950 m	2 958 sh	—	2 958 sh	2 950 sh
—	—	—	—	—	—	2 938 s	—	—
2 932 w	2 926 m	2 928 m	2 926 m	2 925 m	2 930 m	—	2 930 w	2 930 w
—	—	—	—	2 892 sh	—	2 890 sh	2 900 sh	2 895 w
2 882 w	—	—	—	—	—	2 875 sh	—	2 870 sh
—	2 858 w	2 862 w	2 858 w	2 865 w	2 858 w	—	2 860 vw	2 860 sh
—	—	—	—	—	—	2 865 s	—	—
2 810 vw	—	—	2 800 sh	2 801 w	—	2 833 m	2 800 w	—
—	—	—	—	—	—	—	2 780 sh	2 770 vw
—	2 734 w	2 750 vw	2 740 vw	2 759 vw	—	—	2 740 vw	—
—	—	—	—	2 737 w	—	—	—	—
—	2 704 w	2 695 vw	—	2 698 vw	—	2 695 sh	—	—
—	—	—	2 670 sh	—	2 678 w	2 680 sh	2 675 w	2 680 w
—	—	—	—	—	—	2 668 w	—	2 665 w
2 655 w	2 652 w	2 652 vw	2 650 w	2 648 w	—	—	—	—
2 620 sh	2 620 w	2 623 vw	2 625 sh	2 637 sh	—	2 635 sh	—	2 625 vw
—	—	—	2 607 sh	—	—	2 540 vw	2 550 vw	—
—	—	—	—	—	—	2 500 vw	—	—
—	—	—	—	—	—	—	—	—
—	—	—	—	2 458 w	—	—	—	2 455 vw
—	—	—	—	2 423 w	2 420 vw	—	—	—
—	2 390 vw	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	2 275 vw
—	—	—	—	—	—	—	2 245 vw	2 245 vw
—	—	—	—	—	—	—	—	2 150 vw

TABLE II  
(Continued)

Vibrational assignment	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>
	—	—	—	—	—	—
	—	—	—	—	—	—
	2 015 w	2 006 vw	—	—	—	2 005 w
Region of overtone and combination tone bands	1 986 vw	1 987 w	1 985 w	1 995 sh	1 996 w	—
	—	—	—	—	—	—
	1 963 vw	—	1 965 w	1 978 w	1 968 w	1 974 w
	—	1 930 vw	1 940 vw	1 942 vw	1 945 vw	1 933 w
	—	—	—	—	—	—
	—	—	—	—	—	—
	1 900 sh	—	1 893 vw	1 884 w	1 898 vw	1 899 vw
	1 874 vw	1 880 vw	—	—	1 871 w	1 862 w
	—	—	1 857 vw	—	1 855 sh	1 832 vw
	—	—	1 820 vw	1 818 vw	1 825 sh	—
	1 799 vw	—	—	—	1 810 w	1 795 vw
	—	—	—	—	1 801 sh	—
	—	1 763 vw	1 760 w	1 770 sh	1 771 vw	1 768 w
	1 751 vw	—	1 750 w	1 735 sh	1 742 sh	—
	1 736 sh	—	—	—	1 720 sh	—
	1 333 sh	—	—	—	—	—
	1 719 w	—	1 716 sh	1 715 sh	—	1 718 w
	1 705 w	1 697 sh	—	—	1 700 sh	1 696 sh
	—	—	—	—	—	—
Region of ring stretch. bands	—	—	—	—	1 695 sh	—
	1 685 sh	1 685 sh	—	—	—	1 685 sh
C—O stretch.	1 681 vs	1 678 vs	1 675 vs	1 674 vs	1 670 vs	1 669 vs
	—	1 668 sh	—	—	—	—
	—	—	—	—	—	—
Ring stretch.	—	—	—	—	—	—
	1 636 m	1 645 w	—	1 643 sh	—	1 654 sh
	—	—	—	—	—	1 647 sh
Ring stretch.	—	—	—	—	—	1 628 m
	1 624 sh	1 637 w	—	—	1 616 sh	—
	—	—	—	—	1 604 sh	—
Ring stretch.	1 593 vs	1 592 vs	1 595 vs	1 595 vs	1 595 vs	1 597 vs
Ring stretch.	1 583 sh	1 584 sh	1 584 sh	1 585 sh	1 586 sh	—
	—	1 575 w	—	—	—	—

Table II  
(Continued)

VII	VIII	IX	X	XI	XII	XIII	XIV	XV
—	—	—	—	—	—	—	2 090 sh	—
—	—	—	—	—	—	—	2 060 vw	—
2 004 w	—	—	—	2 000 vw	—	—	—	—
—	—	—	—	—	—	1 992 vw	—	1 995 sh
—	—	—	—	—	—	—	—	1 982 w
1 978 w	1 964 m	—	—	—	1 967 w	1 972 w	1 962 w	1 972 sh
1 948 vw	—	1 956 w	1 949 w	1 952 vw	—	1 950 sh	1 950 w'	—
—	—	—	—	—	—	—	1 935 vw	—
—	—	—	—	—	—	—	1 920 vw	—
1 892 vw	1 895 w	1 890 vw	1 902 w	—	1 890 vw	1 894 vw	—	1 892 w
1 867 w	—	—	—	—	—	1 873 vw	1 862 vw	1 855 vw
—	1 830 vw	—	1 853 w	1 852 w	1 846 w	1 860 vw	1 834 w	1 828 w
1 813 w	1 815 vw	—	1 804 w	1 809 w	—	—	1 812 sh	1 816 w
1 792 vw	—	—	1 790 vw	—	—	—	—	—
—	—	—	—	—	—	—	—	—
1 775 vw	—	—	1 760 vw	—	—	1 766 w	1 763 w	—
—	1 752 w	1 755 w	—	1 757 w	1 733 w	—	1 732 vw	—
—	—	—	—	—	—	—	—	1 741 w
—	1 728 w	1 725 w	1 717 sh	—	—	—	—	—
1 718 sh	—	1 708 w	1 701 sh	—	1 704 sh	1 716 sh	—	—
1 701 sh	1 699 sh	—	1 696 sh	1 702 sh	1 698 sh	1 700 sh	1 705 sh	1 702 sh
—	—	—	—	1 685 sh	—	—	—	—
1 695 sh	—	—	—	—	—	—	1 696 sh	1 697 sh
1 685 sh	—	—	1 686 sh	—	—	1 684 sh	1 686 sh	1 687 s
1 676 vs	1 676 vs	1 677 vs	1 676 vs	1 674 vs	1 683 vs	1 681 vs	1 677 vs	1 681 vs
—	—	—	1 670 sh	—	1 677 sh	1 675 sh	—	1 677 sh
1 660 sh	—	1 666 sh	1 664 sh	—	1 669 sh	—	—	1 668 sh
—	—	—	—	—	—	1 663 s	—	—
—	—	1 652 sh	—	—	—	1 653 sh	—	—
1 632 w	—	—	1 638 w	—	—	1 647 sh	—	—
—	—	—	—	1 640 m	1 621 s	—	—	1 643 m
1 616 sh	—	—	—	—	—	1 636 sh	—	1 637 sh
—	—	—	—	—	1 600 sh	—	—	—
1 597 vs	1 602 vs	1 601 vs	1 598 vs	1 597 vs	1 587 vs	1 593 vs	1 616 vs	1 596 vs
—	—	—	—	—	—	—	1 587 s	1 586 sh
1 573 sh	—	—	—	—	1 570 sh	—	—	1 575 sh



TABLE II  
(Continued)

Vibrational assignment	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>
Ring stretch.	—	—	1 573 m	1 569 s	1 563 s	1 559 s
	1 561 sh	1 570 sh	—	—	—	—
	—	1 557 w	—	—	—	—
	—	—	—	—	—	1 543 sh
	—	1 537 w	—	—	1 515 w	1 535 sh
Ring stretch.	1 515 vw	—	—	—	—	—
Ring stretch.	—	1 479 w	—	1 482 w	1 483 w	1 483 vw
Ring stretch.	1 477 m	—	—	—	—	—
	—	—	1 478 vw	—	1 465 sh	—
	—	1 466 sh	—	—	—	—
CH <sub>3</sub> asym. def. and ring stretch resp.	—	1 455 m	1 458 w	1 456 m	1 460 w	1 458 m
CH <sub>2</sub> scissor	—	—	—	—	—	—
	—	—	1 447 vw	1 443 sh	1 453 sh	—
Ring stretch.	1 458 m	1 442 m	—	—	1 441 s	1 441 m
	—	—	—	—	—	1 430 sh
Ring stretch.	—	1 424 s	1 418 m	1 406 m	1 406 s	1 437 sh
	—	—	—	—	—	—
	1 408 vw	1 419 sh	1 405 sh	—	—	—
	—	—	—	—	—	—
CH <sub>3</sub> def. sym.	—	1 384 s	1 387 m	1 386 s	1 384 s	1 384 vs
	1 376 w	—	1 378 sh	—	—	1 363 sh
Ring stretch.	—	—	—	1 378 m	—	—
	—	—	—	—	—	—
Ring stretch.	—	—	—	—	—	—
	—	—	1 338 sh	—	—	—
	1 326 sh	—	—	1 320 sh	1 328 sh	—
Ring stretch.	1 309 s	—	—	—	—	—
	—	—	—	1 298 w	—	1 295 sh
C—C stretch. of —C—(CO)—C—	1 336 vs	1 328 vs	1 329 vs	1 330 vs	1 333 vs	1 330 vs
	1 288 vs	1 273 vs	1 299 vs	1 278 vs	1 282 vs	1 264 vs
Region of CH in-plane bending bonds	—	—	1 273 sh	—	—	—
	—	1 247 s	1 266 s	—	1 261 vs	—
	1 255 sh	—	—	—	—	1 233 sh

TABLE II  
(Continued)

VII	VIII	IX	X	XI	XII	XIII	XIV	XV
—	1 577 m	1 577 s	1 579 sh	1 562 s	—	1 565 m	1 578 s	—
—	1 571 sh	—	1 567 sh	1 558 sh	1 556 sh	1 558 sh	1 557 sh	1 568 sh
—	—	—	—	—	—	1 550 sh	—	1 553 w
—	1 544 w	—	1 543 w	—	—	—	—	—
1 534 sh	1 535 w	1 530 sh	—	1 535 sh	1 535 vw	—	—	—
—	—	—	—	—	1 512 w	—	1 531 m	1 518 w
1 492 sh	1 488 w	1 494 w	1 492 w	—	—	—	1 503 m	1 490 sh
—	—	—	—	—	—	—	1 492 m	1 480 sh
1 480 m	—	—	1 474 sh	1 474 sh	1 473 sh	1 480 w	1 472 sh	—
—	—	—	—	—	—	—	1 466 sh	—
1 460 sh	1 475 sh	1 458 w	1 458 s	1 458 s	—	—	—	—
—	—	—	—	—	—	1 463 m	—	—
—	—	—	—	1 454 sh	—	1 457 sh	—	—
1 452 m	—	—	1 453 s	—	1 463 s	—	1 457 vs	1 468 s
1 439 sh	—	—	1 421 w	—	1 437 sh	—	—	—
—	1 415 s	1 424 m	1 397 sh	—	1 400 s	1 424 s	1 445 vs	1 422 m
—	—	—	—	1 389 sh	—	1 430 sh	—	—
—	—	—	—	—	—	1 420 sh	—	1 419 sh
1 377 sh	—	—	—	—	—	1 384 sh	—	—
1 389 s	1 385 s	1 386 m	1 381 s	1 378 s	—	—	—	—
—	—	—	1 364 w	—	—	1 367 w	—	—
—	—	—	—	—	1 364 m	—	1 397 vs	—
—	—	—	—	—	—	1 360 sh	1 370 sh	1 340 sh
—	—	—	—	1 356 s	—	—	1 379 s	1 350 sh
—	1 353 sh	—	—	1 354 sh	1 344 sh	1 348 sh	1 350 w	—
—	—	—	—	—	—	1 323 sh	—	—
—	—	—	—	—	—	—	1 312 m	—
—	—	—	—	—	1 298 sh	—	1 298 sh	1 313 sh
1 334 vs	1 325 vs	1 330 vs	1 329 vs	1 330 vs	1 329 vs	1 336 vs	1 324 m	1 323 vs
1 299 vs	1 305 vs	1 303 vs	1 306 vs	1 306 vs	1 286 vs	1 294 vs	1 281 vs	1 271 vs
1 280 sh	—	1 294 sh	1 285 sh	1 287 sh	—	1 282 sh	—	—
—	1 270 s	—	1 235 s	—	—	1 255 w	1 240 s	—
1 253 w	1 257 sh	—	—	1 272 sh	1 268 sh	—	1 261 sh	—

TABLE II  
(Continued)

Vibrational assignment	I	II	III	IV	V	VI
1 230 w	1 216 sh	—	—	—	—	1 205 w
—	—	1 212 w	—	—	—	—
1 206 m	1 229 s	1 221 m	1 228 s	1 203 w	—	—
—	—	—	—	—	—	—
—	—	—	—	1 177 vw	—	—
1 172 s	1 187 m	1 179 s	1 189 s	1 160 m	1 171 s	—
1 161 sh	1 175 m	1 165 s	1 162 s	—	—	—
—	1 165 s	1 145 s	—	1 135 s	1 162 s	—
—	—	1 125 vw	—	—	—	1 145 sh
—	1 145 sh	1 108 vw	1 102 w	—	—	1 113 vw
1 098 m	—	—	—	—	—	—
—	1 098 w	1 098 sh	1 075 w	1 100 vw	1 099 vw	—
—	1 093 w	—	—	—	—	—
—	—	—	—	1 055 s	1 075 s	—
1 055 vw	1 072 sh	1 055 vw	1 043 sh	—	—	—
1 035 vw	—	—	—	—	—	—
—	1 039 m	1 044 m	—	1 042 s	1 041 s	—
1 025 sh	1 032 w	1 010 w	—	997 w	1 032 sh	—
—	1 022 m	—	1 021 m	1 030 m	—	—
—	992 sh	—	—	—	—	983 sh
970 m	972 s	970 s	980 s	985 s	976 s	—
—	—	—	970 s	—	—	—
Region of out-of-plane bending bands and skeletal deform. resp.	—	—	—	957 s	—	—
941 vs	—	934 s	945 s	—	—	—
—	937 vw	—	—	—	—	—
913 w	920 m	911 w	925 sh	930 vw	928 w	—
894 w	—	—	906 w	—	896 w	—
—	—	892 m	882 m	900 s	—	—
—	905 w	—	—	—	—	—
—	—	—	—	887 s	—	—
—	—	—	—	875 sh	—	—
—	855 s	852 s	847 s	843 m	852 s	—
—	828 m	—	—	829 sh	827 sh	—
819 s	—	—	820 m	—	824 s	—
—	815 m	814 w	—	822 w	—	—
810 s	808 s	791 m	—	796 s	—	—
—	—	800 sh	792 s	—	799 m	—
790 vw	779 m	—	—	—	—	—
750 sh	732 sh	738 sh	741 sh	—	748 sh	—
—	726 s	711 vs	729 s	728 s	725 vs	—

TABLE II  
(Continued)

VII	VIII	IX	X	XI	XII	XIII	XIV	XV
—	—	1 250 sh	—	1 256 sh	1 238 w	—	1 226 sh	1 213 sh
—	—	1 219 w	—	1 221 sh	—	—	—	—
1 226 s	1 217 m	—	1 217 m	—	1 213 s	1 212 s	—	1 206 m
—	—	—	1 200 s	1 203 s	—	—	—	1 196 sh
—	1 190 w	—	—	1 174 vw	—	—	—	1 171 sh
1 186 m	—	1 180 s	1 175 s	—	1 166 m	1 188 m	1 189 vs	—
1 171 m	—	—	1 150 w	—	—	1 172 w	1 158 w	—
—	1 149 s	—	1 123 m	—	1 144 m	1 161 m	1 149 m	1 159 s
1 154 w	1 099 w	1 141 m	—	—	1 123 sh	—	1 141 sh	1 151 w
—	—	1 117 vw	—	—	—	—	—	—
1 109 m	—	—	—	—	1 108 m	1 102 m	—	1 132 s
—	—	1 094 w	—	—	1 080 vw	1 081 sh	—	1 098 w
—	—	—	—	—	—	1 078 w	—	—
1 071 m	—	—	1 063 m	—	—	—	—	—
—	—	—	1 046 sh	—	—	1 070 sh	—	1 038 w
—	—	—	—	—	—	1 036 w	1 048 w	—
1 025 m	1 044 m	1 042 m	1 028 m	1 031 s	—	—	1 019 m	—
1 004 sh	1 011 w	1 026 w	—	1 014 w	1 013 w	998 w	—	999 sh
—	—	—	—	—	—	—	—	989 sh
—	—	1 010 vw	1 014 sh	998 w	988 sh	974 sh	—	—
—	978 s	980 s	975 s	970 vs	967 vs	962 s	988 vs	974 vs
—	—	—	—	—	—	—	—	979 sh
958 vs	—	—	—	—	—	—	959 s	953 s
—	—	932 s	—	928 s	926 s	939 s	933 s	—
—	933 w	—	924 sh	—	—	—	—	934 sh
911 sh	—	—	—	—	—	—	929 sh	—
—	—	912 w	—	—	—	920 w	—	909 w
901 s	903 m	—	911 s	909 s	—	883 m	917 s	—
862 vw	—	900 sh	—	—	—	—	900 vw	901 w
—	874 s	—	—	—	—	—	—	—
850 vw	—	—	—	—	—	867 vw	858 w	875 vw
—	854 s	858 s	845 s	—	—	—	—	—
816 w	—	834 sh	—	—	—	—	—	826 w
—	—	—	—	—	—	823 m	—	—
—	—	—	815 m	—	—	816 sh	—	—
800 s	—	—	—	—	806 m	—	—	—
—	—	813 w	—	—	797 sh	795 sh	809 sh	808 sh
—	—	—	782 w	—	—	787 m	—	—
754 w	—	775 w	751 m	—	756 vs	745 sh	766 vs	787 s
—	773 s	732 vs	737 vs	742 s	—	—	—	—

TABLE II  
(Continued)

Vibrational assignment	I	II	III	IV	V	VI
	720 w	—	—	—	—	—
	—	705 vs	—	715 vs	714 vs	—
	—	—	691 vw	—	—	696 vw
	695 vs	—	—	—	—	—
Region of skeletal deform.	673 sh	688 sh	669 vw	664 sh	676 w	—
	—	—	—	—	—	—
	—	—	—	—	—	—
	—	655 s	656 s	653 m	656 s	654 m
	—	—	640 sh	—	—	—
	623 s	621 m	637 s	616 m	643 s	623 sh
	—	—	—	—	—	605 m
	—	—	580 s	601 w	581 s	—
	—	547 w	—	570 sh	—	—
	538 vw	542 sh	—	550 w	546 w	—
	—	—	—	—	—	—
	—	—	—	534 vw	538 w	536 s
	—	503 m	518 s	—	504 s	—
	—	487 w	—	—	482 w	—
	—	—	—	490 m	—	—
	472 w	476 sh	473 vw	463 w	463 vw	469 sh
	—	—	—	—	—	463 m
	—	—	—	—	—	—
	—	440 vw	442 w	438 w	439 w	—
Skeletal deform.	407 sh	—	425 vw	419 sh	413 sh	419 sh
	388 s	401 s	390 s	388 s	399 s	400 s
	—	—	—	—	—	—
	—	—	—	—	—	—
	—	—	372 sh	—	371 vw	368 sh
	—	—	—	—	—	—
	—	—	336 w	330 w	—	—
	—	—	290 w	302 w	306 w	323 w

## Measurement of Infrared Spectra

The infrared spectra were measured with a Beckman IR-7 double-beam grating spectrophotometer in the regions of 250–600 and 600–4000  $\text{cm}^{-1}$ . With respect to the fact that most samples were insoluble in solvents suitable for the infrared spectroscopy, the samples were measured in solid phase by using the technique of KBr pellets. As the absorption bands of CO vibrations and C—C stretching vibrations of the C—CO—C atom grouping are very intense, the spectra had to be measured, besides commonly used concentrations (about 3 mg sample/300 mg KBr) also at lower concentrations (about 0.1–1 mg sample/300 mg KBr).

TABLE II  
(Continued)

VII	VIII	IX	X	XI	XII	XIII	XIV	XV
732 sh	—	719 sh	—	734 sh	728 sh	731 m	730 w	745 w
717 vs	714 s	—	716 s	—	713 vs	717 vs	—	705 vs
692 vw	—	700 w	—	718 m	—	—	724 w	724 sh
—	—	—	—	—	—	—	711 m	—
669 w	670 sh	668 sh	—	—	683 vw	685 vw	669 sh	668 w
—	—	—	—	—	—	669 w	666 w	—
663 sh	—	—	—	—	661 w	663 w	—	—
—	655 s	656 vs	670 m	—	—	—	—	—
—	—	—	—	—	630 vw	—	—	—
617 s	—	—	645 s	—	—	608 s	625 m	624 m
—	594 vw	—	—	—	—	—	—	—
—	—	591 s	594 s	596 s	575 s	—	—	—
570 w	—	—	562 sh	—	—	—	578 w	—
—	—	—	—	588 sh	—	559 w	555 sh	—
—	545 s	—	566 s	569 m	—	—	—	—
—	532 s	533 w	—	—	—	—	539 vs	527 sh
—	—	—	—	—	—	—	—	519 s
—	—	—	—	—	—	495 vw	517 w	—
—	—	474 s	487 m	—	470 s	—	479 vs	—
461 w	474 vw	467 sh	474 vw	—	—	462 w	—	473 w
—	—	—	—	—	—	—	—	—
—	—	—	459 w	—	—	—	—	—
440 w	—	438 vw	445 w	—	—	439 w	—	449 s
—	410 w	—	—	—	—	—	—	425 w
416 m	387 s	428 m	421 m	432 s	386 s	417 m	—	399 m
—	—	406 vw	398 sh	388 sh	—	—	395 w	383 sh
386 s	—	385 s	381 s	373 s	—	384 s	—	376 s
369 w	—	—	369 w	—	—	333 w	—	—
—	360 s	356 m	361 m	—	—	328 sh	354 s	—
—	—	—	340 w	—	—	325 sh	—	—
330 m	—	—	—	—	—	303 vw	—	—

## RESULTS AND DISCUSSION

Frequencies of infrared bands from the region  $4000-200\text{ cm}^{-1}$  together with some comments concerning vibrational assignment are given in Table II. Frequencies of characteristic vibrations are printed in italics.

Quinones were subjected to spectral measurements in the form of KBr pellets. With a few exceptions all spectra show a broad absorption band near  $3330\text{ cm}^{-1}$  due to the absorbed humidity; only 1,3-dimethylantraquinone and pentacene-6,13-

quinone pellets, when dried over  $P_2O_5$  *in vacuo*, gave unperturbed spectra. There are no more bands due to the absorbed humidity in the infrared spectrum besides that at  $3330\text{ cm}^{-1}$ .

When compared with polynuclear hydrocarbons<sup>30</sup>, the related quinones show infrared spectra composed of bands the assignment of which is much more difficult; there is only little known about the analyses of spectra of quinones. That is why the infrared spectra of polynuclear quinones need some comments.

### *Vibrations Related to Quinoid Arrangement*

The spectra of all compounds measured in this work show a rather intense band between  $1683\text{--}1669\text{ cm}^{-1}$  assigned to the stretching vibration of quinone carbonyls. Unfortunately, the frequencies of the  $\nu(\text{C}=\text{O})$  band are affected by intermolecular forces operating in KBr pellets; this makes any structure-spectrum correlation useless. Let us only say that all quinones not substituted by the methyl groups show the  $\nu(\text{C}=\text{O})$  frequencies in a narrower range of  $1683\text{--}1677\text{ cm}^{-1}$ .

Two rather intense bands, found always between  $1340\text{--}1260\text{ cm}^{-1}$  (about  $40\text{ cm}^{-1}$  distant) are also very characteristic for polynuclear quinones. Both the bands seem to represent the C—C stretching vibrations of the quinoid C—CO—C grouping coupled with the C=O stretch<sup>5</sup>.

Infrared spectra of polynuclear quinones show a very strong band in the region  $1616\text{--}1587\text{ cm}^{-1}$  together with a medium one between  $1512\text{--}1477\text{ cm}^{-1}$ ; in simpler case, the former one is assigned to the ring-stretching vibration coupled with the C=O stretch<sup>5</sup>. In more complicated quinone molecules the assignment becomes more complicated due to the fact that the vibrations of any aromatic ring system occur ordinarily around  $1600$  and  $1500\text{ cm}^{-1}$ .

### *Ring-Hydrogen Vibrations*

For compounds with such a complicated structure as in the case of polynuclear quinones the interpretation of the  $\nu(\text{C—H})$  stretching region becomes rather complicated. The analysis of the in-plane and out-of-plane vibrations seems to be easier.

In-plane bending vibrations of aromatic hydrogens occur ordinarily between  $1300\text{--}1000\text{ cm}^{-1}$ ; out-of-plane vibrations show bands below  $1000\text{ cm}^{-1}$  in most cases. In the infrared spectra of polynuclear quinones there are strong to medium intense bands of the in-plane bending vibrations between  $1250\text{--}1200\text{ cm}^{-1}$ ,  $1190\text{--}1095\text{ cm}^{-1}$  and  $1070\text{--}970\text{ cm}^{-1}$ . Also the bands of the out-of-plane bending vibrations in the spectra of polynuclear quinones lie in the positions expected; unfortunately, and in contradistinction to polynuclear hydrocarbons<sup>30</sup>, their frequencies do not correlate with the structure of their molecules (see also refs<sup>31,32</sup>). For instance the band of the out-of-plane vibration, found in the spectrum of anthraquinone at

819  $\text{cm}^{-1}$ , is significantly out of ordinary range characteristic of systems with four adjacent hydrogen atoms in one benzene ring.

### *Vibrations of the Methyl Group*

As seen from Table II, the frequencies of the methyl group vibrations show rather constant values. Owing to a high characteristicity of some of these vibrations, their frequencies in Table II are italicized.

#### REFERENCES

1. Josien M. L., Fuson N., Lebas J. M.: *Phys. Rev.* **87**, 170 (1952).
2. Fuson N., Josien M. L., Gregory T. M.: *Phys. Rev.* **87**, 170 (1952).
3. Tanaka O.: *Chem. Pharm. Bull. (Tokyo)* **6**, 24 (1958).
4. Tanaka O.: *Chem. Pharm. Bull. (Tokyo)* **6**, 18 (1958).
5. Hadži D., Sheppard N.: *J. Am. Chem. Soc.* **73**, 5460 (1951).
6. Bellamy L. J.: *The Infrared Spectra of Complex Molecules*, p. 129. Methuen, London 1956.
7. Fieser L. F., Heymann H.: *J. Am. Chem. Soc.* **64**, 376 (1942).
8. Fieser L. F. in *Organic Syntheses*, Coll. Vol. I, p. 353. Wiley, New York 1932.
9. Elbs K., Günther M.: *Ber.* **20**, 1364 (1887).
10. Heller G.: *Ber.* **43**, 2890 (1910).
11. Fairbourne A.: *J. Chem. Soc.* **119**, 1574 (1921).
12. Mellier M. T.: *Ann. Chim. (Paris)* **19**, 666 (1955).
13. Schroeter G.: *Ber.* **54**, 2242 (1921).
14. Rubidge C. R., Qua N. C.: *J. Am. Chem. Soc.* **36**, 732 (1914).
15. See 8, p. 517.
16. Smith M. E.: *J. Am. Chem. Soc.* **43**, 1920 (1921).
17. Clar E., John F., Hawran B.: *Ber.* **62**, 940 (1929).
18. Scholl R., Donat, J.: *Chem. Ber.* **64**, 318 (1931).
19. Badger G. M., Cook J. W., Goulden F.: *J. Chem. Soc.* **1940**, 16.
20. Alder K., Stein G., Pries P., Winckler H.: *Ber.* **62**, 2337 (1929).
21. Morgan G. T., Coulson E. A.: *J. Chem. Soc.* **1931**, 2323.
22. Allen C. F. H., Bell A. in *Organic Syntheses*, Coll. Vol. III, p. 310. Wiley, New York 1955.
23. Ried W., Anthöfer F.: *Angew. Chem.* **65**, 601 (1953).
24. Bruckner V., Karczag-Wilhelms K., Körmendy K., Mészáros M., Tomasz J.: *Acta Chim. Acad. Sci. Hung.* **22**, 444 (1960).
25. Mills W. H., Mills M.: *J. Chem. Soc.* **101**, 2194 (1912).
26. Waldmann H., Mathiowetz H.: *Ber.* **64**, 1713 (1931).
27. Grinev A. N., Ermakova V. N., Terent'ev A. P.: *Ž. Obšč. Chim.* **29**, 90 (1959).
28. Lora-Tamayo M., Leon J. L.: *J. Chem. Soc.* **1948**, 1499.
29. Gaylord N. G., Štěpán V.: *J. Org. Chem.*, in press.
30. Vodehnal J., Štěpán V.: *This Journal*, in press.
31. Danneberg H., Naerland A.: *Z. Naturforsch.* **12b**, 1 (1957).
32. Wiberley S. E., Gonzales R. D.: *Appl. Spectry* **15**, 174 (1961).
33. Kempf R.: *J. Prakt. Chem.* **78**, 257 (1908).
34. Morgan G. T., Coulson E. A.: *J. Chem. Soc.* **1929**, 2203.
35. Morgan G. T., Coulson E. A.: *J. Chem. Soc.* **1929**, 2551.

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