Spectroscopic Studies of 1, 2- and 3, 4-Phthaloylacridones

By Takayuki HAYASHI and Jun-ichirō MAEHARA*

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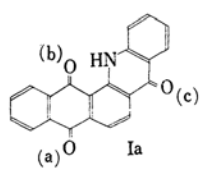
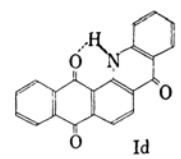
Phthaloylacridones are compounds of a high melting point and a low solubility in organic solvents. 1, 2-Phthaloylacridone, quite similar to acridone in its orange color, is a relatively strong acid which dissolves in alcoholic potassium hydroxide with a violet color[1]. The *N*-methyl derivative is non-acidic, more soluble in organic solvents, and lower-melting than 1, 2-phthaloylacridone, the properties of which are probably the result of intermolecular hydrogen bonding[2]. 3, 4-Phthaloylacridone is similar to 1-phenylaminoanthraquinone in its red-violet color, which indicates that its molecule exists in a true acridone, not a hydroxyacridone, structure, and it is lower-melting and more soluble in organic solvents than isomeric 1, 2-phthaloylacridone, suggesting the occurrence of intramolecular hydrogen bonding[2]. As the infrared, visible and ultraviolet regions of the spectra might yield more interesting information, it seemed desirable to investigate the spectra of these phthaloylacridones and their related compounds.

Results and Discussion

Visible Absorption Spectra.—For 1-benzoylaminoanthraquinone, a IIIb structure has been largely discredited[3]; also, its molecule could not exist in structure IIIc, since amide-type resonance is not possible for IIIc[4]. 1-Benzoylaminoanthraquinone is the resonance hybrid of the forms IIIa, IIId and IIIe[4]. The phthaloylacridones are chemically closely similar to the acylaminoanthraquinones[5], and 3, 4-phthaloylacridone is a vinylog of 1-benzoylaminoanthraquinone. It seems probable, therefore, that the molecule of the former can not exist in either the structure Ib or Ic, that the former is the resonance hybrid of the forms



Ia



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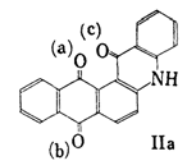
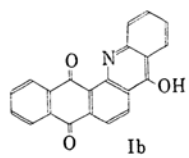
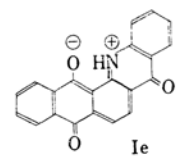


IIa



Ib



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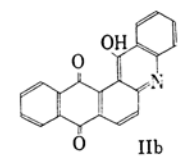

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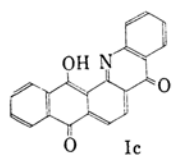

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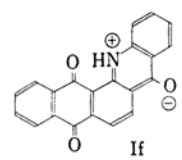

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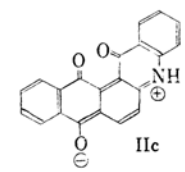


IIc

* Present address: The Research Laboratory of Idemitsu Kōsan Co., Tokuyama-shi.

1) F. Ullmann and P. Ochsner, *Ann.*, **381**, 1 (1911); F. Ullmann and M. Sone, ibid., **380**, 336 (1911); T. Maki and K. Eguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kōgyō Kagaku Zassi*), **44**, 788 (1941).

2) W. Bradley and H. Kiwar, *J. Chem. Soc.*, **1960**, 2859.

3) L. Valentine, *J. Soc. Dyers & Colorists*, **72**, 286 (1956).

4) T. Hayashi and R. Shibata, This Bulletin, **34**, 1116 (1961).

5) W. Bradley, "Recent Progress in the Chemistry of Dyes and Pigments", The Royal Institute of Chemistry, London (1958), p. 4.

TABLE I. VISIBLE ABSORPTION PEAKS OF SUBSTITUTED AMINOANTHRAQUINONES AND PHTALOYLACRIDONES

	In *o*-dichloro-benzene	In pyridine	In conc. sulfuric acid
Anthraquinone			410 (7400)[8]
1-Aminoanthraquinone	466 (5980)*		380 (6000)[9]
2-Aminoanthraquinone	413 (3800)		375 (7100)[9]
1-Phenylaminoanthraquinone	508 (5920)		
1-Aminoanthraquinone-2-carboxylic acid	495 (7900)		355 (3300)
1-(*o*-Carboxyphenyl)-aminoanthraquinone	500 (6600)		370 (4100)
1-Benzoylaminoanthraquinone	421 (5900)[4]	415 (6350)[7]	
1,2-Phthaloylacridone		400 (11300)[2]	385 (7900)
			505 (11800)
3,4-Phthaloylacridone	516 (8000)[2]	516 (8000)[2]	365 (7200)**
			465 (3890)
5,6-Phthaloyl-1,2-benzacridone	515 (9000)[2]		

* Wavelength, mμ (molar extinction coefficient)
** The peak in 94% sulfuric acid appeared at 365~370 mμ[10].

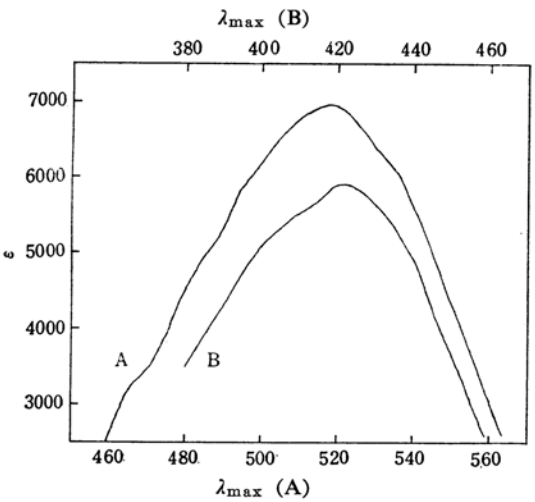


Fig. 1. Visible absorption spectra.
A: 3,4-Phthaloylacridone
B: 1-Benzoylaminoanthraquinone

Ia, Ie and If and that the carbonyl group in the nitrogen-bearing ring for the former shows an insulating effect similar to that in the benzoylamino group for the latter[4]. Their spectra in the visible region are shown in Fig. 1. As in the case of 5,6-phthaloyl-1,2-benzacridone[6], 3,4-phthaloylacridone gives a absorption curve broadly similar to that of 1-benzoylaminoanthraquinone, illustrating the insulating effect of the carbonyl group in the nitrogen-bearing ring. Such a fact is consistent with the above-mentioned deduction that both visible absorption bands are due to the same chromophore.

As is indicated in Table I, a comparison of the peaks of 3,4-phthaloylacridone and 1-benzoylaminoanthraquinone indicates a bathochromic shift of 95 mμ; the peak of the former shifts towards a longer wavelength than those of 1-aminoanthraquinone-2-carboxylic acid and 1-(*o*-carboxyphenyl)- and 1-phenyl-aminoanthraquinones. This fact can probably be attributed to the increased coplanarity of the molecule owing to the existence of the nitrogen-bearing ring for 3,4-phthaloylacridone. This interpretation is supported by the following thesis: the coplanarity on the molecule of 5,6-phthaloyl-1,2-benzacridone should be the same degree as for 3,4-phthaloylacridone, and therefore the effective area of the π-electron system[11] seems to be larger for the former than for the latter. As is clear from the results in Table I, the peak of the former appears at the same wavelength as for the latter, and the intensity is greater for the former than for the latter.

This fact is also deduced from the following results: though a comparison of the peaks of 3,4-phthaloylacridone and 1-aminoanthraquinone indicates a bathochromic shift of 53 mμ, that of 1,2-phthaloylacridone and 2-aminoanthraquinone makes only a slight hypsochromic shift of 13 mμ. For 1-amino-, 1-benzoylaminoanthraquinones[4,12] and 1,1'-dianthrimide[8], mesomeric shifts in their chromophoric systems contributed mainly to the shifts of their absorption peaks. Therefore, as will be clear from the results of the study of the infrared

6) J. J. Moran and H. I. Stonehill, *J. Chem. Soc.*, **1957**, 765.
7) R. H. Peters and H. H. Sumner, ibid., **1953**, 2101.
8) R. A. Durie and J. S. Shannon, *Australian J. Chem.*, **11**, 189 (1958).
9) K. A. Durie and J. S. Shannon, ibid., **11**, 168 (1958).
10) A. M. Lukin, P. M. Aronovich and G. P. Brin, *Zhur. Obshchei Khim.*, **20**, 2219 (1950); *Chem. Abstr.*, **45**, 7124 (1951).
11) E. A. Braude, *J. Chem. Soc.*, **1950**, 379; R. H. Peters and H. H. Sumner, *J. Soc. Dyers & Colorists*, **71**, 130 (1955).
12) G. S. Egerton and A. Roach, ibid., **74**, 401 (1958).

spectra of 3, 4-phthaloylacridone, the carbonyl group is hydrogen-bonded with the imino group, though probably hydrogen bonding is not the main cause of such a large difference between the shifts of 3, 4- and 1, 2-phthaloylacridones. Such a hypsochromic shift of the peak for 1, 2-phthaloylacridone is, therefore, to be attributed to the reduced mesomeric shift, leading to the IIc structure, owing to the decreased coplanarity of the molecule, which is due to the repulsion between two vicinal carbonyl-type oxygen atoms.

In aminoanthraquinones and phthaloylacridones, the protonation of their carbonyl oxygen atoms can occur, but it is not possible to say positively whether one, two or three carbonyl oxygen atoms are protonated[9,13]. As is indicated in Table I, the peaks of 1- and 2-aminoanthraquinones in concentrated sulfuric acid are shifted to shorter wavelengths and lower intensities compared with anthraquinone, and appear at shorter wavelengths than those in organic solvents. These hypsochromic shifts are most probably caused by the protonation of the amino group. On the contrary, as is indicated in Table I, 1, 2-phthaloylacridone absorbs at a greatly longer wavelength in concentrated sulfuric acid than in pyridine. Similar phenomena were also seen in indanthrone. The absorption peaks of indanthrone appeared at 371, 422, 482, 554, 598 and 635 mμ in ethanol[6], at about 620, 675 and 740 mμ in 1, 2, 4-trichlorobenzene[14], and at 390, 462 and 818 mμ in concentrated sulfuric acid[8]. Its absorption peak at the longest wavelength indicates a marked bathochromic shift at the last. Furthermore, in concentrated sulfuric acid indanthrone absorbed at longer wavelengths than did 1, 2-diaminoanthraquinone. This fact was attributed to the strong amide-type resonance in the former persisting in concentrated sulfuric acid and to the inhibited protonation of the imino groups, though the amino groups of the latter were protonated[8]. On the contrary, since the phthaloylacridones are chemically closely similar to the acylaminoanthraquinones[5], the amide-type resonance for the former is not so strong as for indanthrone; therefore, the protonation of the imino nitrogen atoms of the former can occur. Consequently, the absorption peak at the longest wavelength in concentrated sulfuric acid for 1, 2- and 3, 4-phthaloylacridones should be attributed to the production of new chromophoric systems by protonation. In concentrated sulfuric acid, two absorption peaks of 1, 2-phthaloylacridone appear at respectively longer wavelengths than do corresponding ones of 3, 4-phthaloylacridone, but in pyridine the reverse is found to be true.

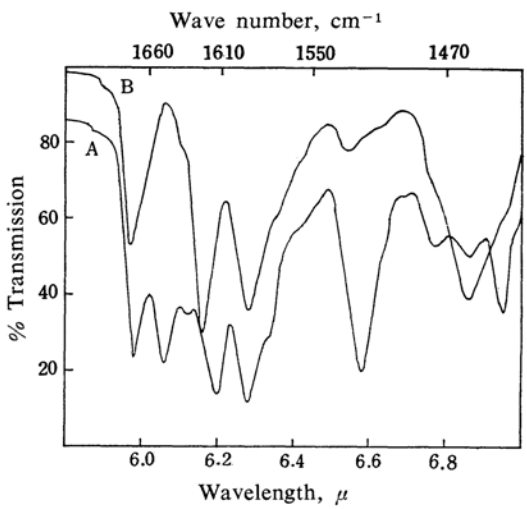


Fig. 2. 6 μ-Region of infrared absorption spectra.

A: 3, 4-Phthaloylacridone
B: 1, 2-Phthaloylacridone

TABLE II. 3 AND 6 μ-BANDS OF SOLID SUBSTITUTED ANTHRAQUINONES AND PHTHALOYLACRIDONES

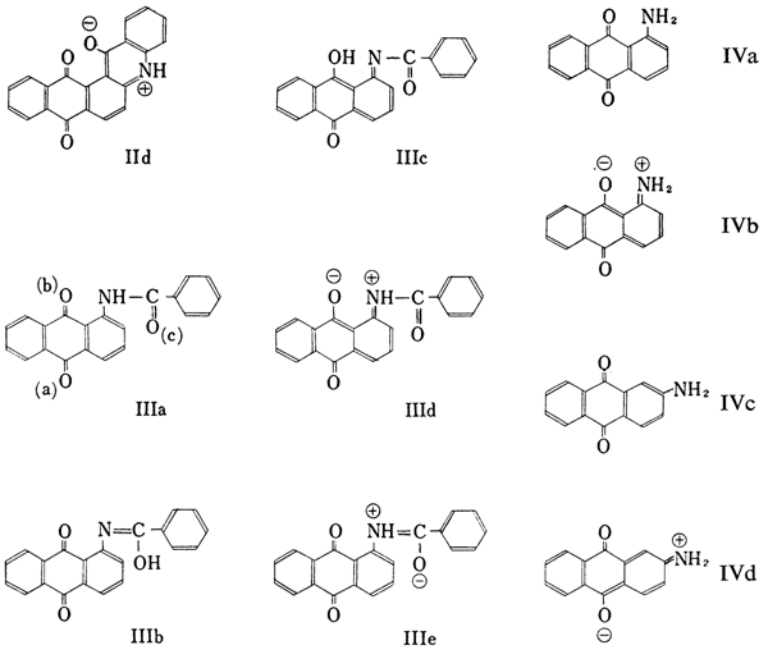
	3 μ-Bands, cm^{-1} (NH frequencies)	6 μ-Bands, cm^{-1} (C=O frequencies)		
		(a)	(b)	(c)
Anthraquinone[15]		1676		
1-Aminoanthraquinone[15]	3420, 3330	1665	1612	
2-Aminoanthraquinone[15]	3470, 3330, 3220	1676	1625	
1-Benzoylaminoanthraquinone[4]	3175	1681	1669	1637
1, 2-Phthaloylacridone*	3300, 3215	1675	1675	1623
3, 4-Phthaloylacridone*	3226, 3195	1672	1650	1613
5, 6-Phthaloyl-1, 2-benzacridone	3236	1678	1656	1608

* The C=O(a), (b) and (c) frequencies for 1, 2- and 3, 4-phthaloylacridones were observed at 1675, 1675 and 1623, and at 1672, 1653 and 1618 cm^{-1}, respectively, by the potassium bromide disk technique.

13) R. A. Hebert, M. B. Goren and A. A. Vernon, *J. Am. Chem. Soc.*, **74**, 5779 (1952); A. Geake, *Trans. Faraday Soc.*, **37**, 68 (1941).

14) J. Weinstein and C. Merritt, *J. Am. Chem. Soc.*, **81**, 3759 (1959).

15) M. S. C. Flett, *J. Chem. Soc.*, **1948**, 1441.



This bathochromic shift is probably due to the fact that, since the molecule of the former has a decreased coplanarity compared with the latter, the reduced effect of the strongly electron-attracting $-NH_2^+-$ group contributes to the resonance hybrid.

Infrared Absorption Spectra.—Three and six μ bands of aminoanthraquinones and phthaloylacridones suspended in Nujol are shown in Table II, and the spectra in the 6 μ region of the latter are shown in Fig. 2. As 3, 4-phthaloylacridone is a vinylog of 1-benzoylaminoanthraquinone, the 1672, 1650 and 1613 cm^{-1} bands for the former are assigned, respectively, to vibrations of the C=O(a), C=O (b) and C=O(c) groups indicated in Ia, similar to those of the latter[4,16]. In the same manner, the 1675 cm^{-1} band for 1, 2-phthaloylacridone is assigned to vibrations of both the C=O(a) and C=O(b) groups indicated in IIa, and the 1623 cm^{-1} band, to the vibration of the C=O(c) group. In such unsymmetrically substituted anthraquinones as amino- and hydroxy-derivatives, two bands appear, since the strengths of the two C=O bonds are unequal, but unsymmetrically substituted anthraquinones such as nitro-, chloro-, methoxy- and methyl-derivatives, on which the absorption peaks hardly appear in the visible region, give a single C=O frequency, since the dissymmetry is insufficient for two separate bands to be observed[15]. Therefore, two carbonyl groups of the anthraquinone nucleus for 1, 2-phthaloylacridone, the visible absorption peak of which appears at 400 mμ, seem to give only one band in the infrared region. On the contrary, those of 3, 4-phthaloylacridone, the visible absorption peak of which appears at 516 mμ, give two bands. Its C=O(c) frequency agrees with the C=O(b) frequency of 1-aminoanthraquinone IVa, and a relation between If and IVb for them corresponds to that between the IId of 1, 2-phthaloylacridone and the IVd of 2-aminoanthraquinone. It is probable, therefore, that the frequency at 1623 cm^{-1} for 1, 2-phthaloylacridone, being equal to the C=O(b) frequency for 2-aminoanthraquinone, may be assigned to the vibration of the C=O(c) group. Such facts about the C=O frequencies of 1, 2-phthaloylacridone are to be attributed to the reduced mesomeric shift leading to the IIc structure owing to the above-mentioned decreased coplanarity of the molecule. This interpretation is supported by the fact that the C=O(c) frequency of 1, 2-phthaloylacridone is about the same as for *N*-methyl-γ-quinolone[17], the C=O frequency of which appeared at 1625 cm^{-1}.

The absorption of both the 1, 2- and 3, 4-phthaloylacridones obtained using the potassium bromide disk technique occurred at 1580 cm^{-1}. Frequencies for the C=N groups[18] are most probably found in the frequency range 1690 to 1640 cm^{-1}, and the influence of conjugation is usually small. The observed frequencies in

16) T. Hayashi. *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1985 (1960).

17) P. I. Ittyerah and F. G. Mann, *J. Chem. Soc.*, **1958**, 467.

18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley & Sons, Inc., New York (1958), p. 267.

phthaloylacridones at 1580 cm^{-1} appear, therefore, at too low a frequency to be normally attributed to the C=N vibration. Furthermore, when C=N and C=C groups are in conjugation, particularly in cyclic systems, it is doubtful whether either group can be regarded as retaining its individual character; therefore, the assignment of C=N frequencies under such circumstances is not reliable[18]. The 1575 cm^{-1} band for 1, 1'-dianthrimide was not attributed to the C=N vibration, but to the ring vibration[8]. The 1582 cm^{-1} band for 1-benzoylaminoanthraquinone was also attributed to the ring vibration[16]. Furthermore, since not only amino-substituted anthraquinones, indanthrones, and anthraquinoneazines, but also anthraquinone, had medium to strong bands in the vicinity of 1587 cm^{-1}, the 1580 cm^{-1} band of indanthrone could not be reasonably assigned to the C=N vibration; these bands were, rather, attributed to ring vibrations[14]. Thus, there is no precedent for assigning the 1580 cm^{-1} band of phthaloylacridones to the C=N vibration; it also is probably to be assigned to the ring vibration. Consequently, this band can not be used to support the structures containing the C=N bond (Ib, Ic, IIb). This interpretation of the molecular structure in a solid is the same as the deduction on that in solution on the basis of the results of the visible absorption; moreover, chemical evidence does not favor the Ib, Ic and IIb structures.

The spectra in the 3 μ region of 1, 2- and 3, 4-phthaloylacridones mulled in Nujol are shown in Fig. 3. The frequencies for the O–H groups are usually found in the frequency range of 3450~3650 cm^{-1}, and the influence of conjugation is quite large[19]. Many of the frequencies for O–H groups of oxanthrone, anthraquinol and their substituted derivatives in a solid[15] were found in the 3300~3500 cm^{-1} frequency range. Moreover, neither the 3175 cm^{-1} band of 1-benzoylaminoanthraquinone nor the 3165 cm^{-1} band of indanthrone was assigned to the O–H vibration; rather, both were assigned to the N–H vibration[4,14]. For indigo and 5, 5', 7, 7'-tetrabromoindigo, in which an amide-type resonance contributes greatly to their resonance hybrids, the 3268 cm^{-1} band for the former and the 3367 cm^{-1} band for the latter were both assigned to the N–H vibration[20]. Broad and distinct bands at 3226 and 3195 cm^{-1} for 3, 4-phthaloylacridone may appear, therefore, at too low a frequency to be normally assigned to the O–H vibration; therefore, this band can not be used to support

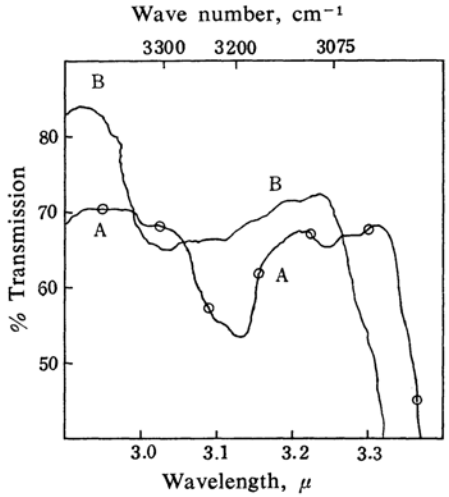


Fig. 3. 3 μ-Region of infrared absorption spectra.
A: 3,4-Phthaloylacridone
B: 1,2-Phthaloylacridone

the structures Ib and Ic. Consequently, the 3195 cm^{-1} band should be assigned to the N–H vibration of the true acridone structure. This interpretation of the molecular structure in a solid is the same as the deduction on that in solution on the basis of the results of the visible absorption; moreover, chemical evidence favors the true acridone structure. According to this view, the molecules of 1, 2-phthaloylacridone should also exist in a true acridone structure, in a way similar to that of the 3, 4-phthaloylacridone molecules.

It may be clearly seen in Fig. 3 that 1, 2-phthaloylacridone has two bands at 3300 and 3215 cm^{-1}. 2-Naphthylamine and 2-aminoanthraquinone in a solid gave a triple N–H band; therefore, these phenomena might not be attributable to the C=O group, but to intermolecular interactions between NH_2 groups[15]. 1-Benzoylaminoanthraquinone as a potassium bromide disk[16] also gave a double N–H band at 3226 and at 3115 cm^{-1}. Both of two bands for 1, 2-phthaloylacridone, therefore, may be attributed to the N–H vibration; therefore, the 3215 cm^{-1} band is assigned to the intermolecularly hydrogen-bonded N–H vibration. It is not possible, however, to state whether or not the occurrence of the 3300 cm^{-1} band is caused by intermolecular interaction between NH groups. The frequencies and broad shapes of the two N–H bands of 3, 4-phthaloylacridone at 3226 and 3195 cm^{-1}, similar to those of 1-benzoylaminoanthraquinone as Nujol mull[16], indicate some degree of hydrogen bonding. This view is supported by the fact that acridone in a carbon tetrachloride solution[21] gives a

19) L. J. Bellamy, ibid., p. 96.
20) G. M. Wyman, *J. Am. Chem. Soc.*, **78**, 4599 (1956); W. R. Brode, E. G. Pearson and G. M. Wyman, ibid., **76**, 1034 (1954).
21) A. V. Karyakin and A. V. Shablya, *Doklady Akad. Nauk S. S. S. R.*, **116**, 969 (1957); *Chem. Abstr.*, **52**, 4324 (1958).

N–H band at 3440 cm^{-1}. The proximity of the C=O and NH groups and the possibility for the formation of a six-membered ring suggest that one bonding is intramolecular, as is indicated in Id. Furthermore, 1-benzoylaminoanthraquinone as Nujol mull[16] gave a intramolecular N–H band at 3175 cm^{-1}, and the frequency of 3, 4-phthaloylacridone at 3226 cm^{-1} is in the vicinity of the intermolecular hydrogen-bonded N–H frequency of 1,2-phthaloylacridone at 3215 cm^{-1}. Therefore, the 3226 and 3195 cm^{-1} bands are most probably to be assigned to intermolecularly and to intramolecularly hydrogen-bonded N–H vibration respectively. This view is supported by the general tendency that, for β-amino-α, β-unsaturated ketones, the intramolecular hydrgen-bonded N–H bands occur at lower frequencies than the intermolecular hydrogen-bonded N–H bands[22]. The extent of conjugation between the imino and the C=O group in the nitrogen-bearing ring should be higher for *N*-phenylacridone than for 3, 4-phthaloylacridone, but the C=O frequency of the latter is lower than that of the former[23], this being 1632 cm^{-1}. This lowering seems also to be caused by intermolecular interaction between the NH and the C=O group for the latter.

22) J. Weinstein and G. M. Wyman, *J. Org. Chem.*, **23**, 1618 (1958).
23) E. R. H. Jones and F. G. Mann, *J. Chem. Soc.*, **1958**, 294.

Experimental

Materials and Apparatus.—The compounds used in this investigation were purified by repeated crystallization and then by chromatography or hot chromatography on alumina in suitable solvents.

The visible absorption spectra were obtained by a Shimadzu spectrophotometer type QB-50. The infrared absorption spectra were obtained using the Nujol mull technique; a Perkin-Elmer Model 21 double beam spectrophotometer fitted with a rock-salt prism was also used. *o*-Dichlorobenzene was purified by the method recommended for monochlorobenzence[24].

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Department of Chemistry
Faculty of Literature and Science
Yamaguchi University
Ushirogawara, Yamaguchi-shi

24) A. Weissberger and E. S. Proskauer, "Organic Solvents", Interscience Publishers, New York (1955), p. 407.