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CHEMISTRY

Further Remarks on the Structure of Aniline Black on the Basis of Infra-Red Absorption Spectra

by

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Continuing our experiments on the structure of emeraldine and aniline black previously reported [1], we have now examined the infrared absorption spectra of the compounds: emeraldine pernigraniline (aniline black), ungreenable aniline black, anilinoquinone, dianilinoquinone and phenazine.

All these compounds have been examined in the Hilger single beam spectrophotometer with optics of sodium chloride. All compounds were used in the form of mull in paraffin oil, the ratio of the substance to the oil being 1/20. The thickness of the layer was 0.02 mm.

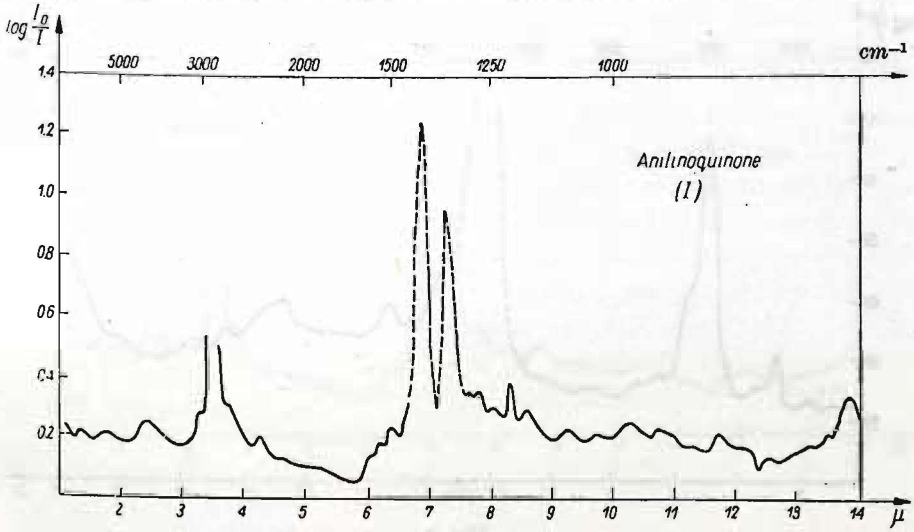

Fig. 1

The results are tabulated below and the absorption curves are reproduced in Fig. 1-6.

All absorption spectra of the compounds (I)—(V) show great similarity in the whole region examined.

The absorption spectrum of phenazine (VI) is similar to those of compounds (I)—(V) in the range from 1 μ to c. 10 μ. From c. 10 μ to 14 μ the absorption curve of phenazine is distinctly different from those of anilinoquinones (I)—(II) and of the products of various stages of formation of aniline black (III—V.)

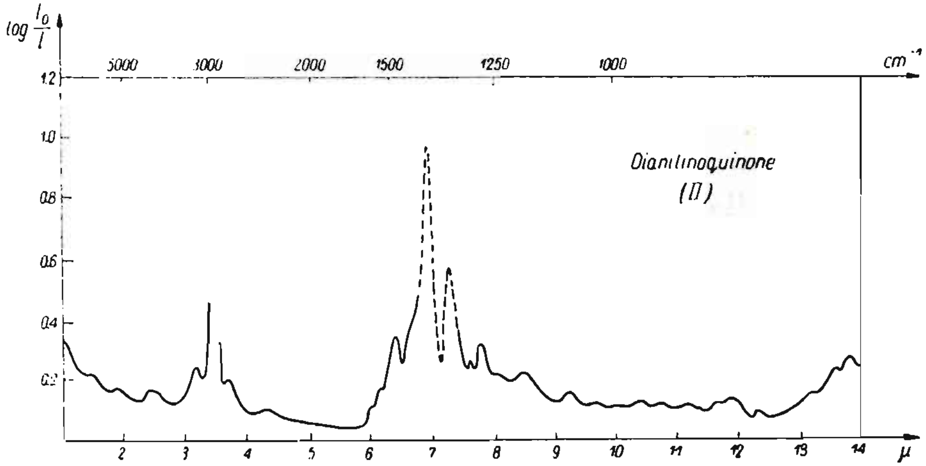

Fig. 2

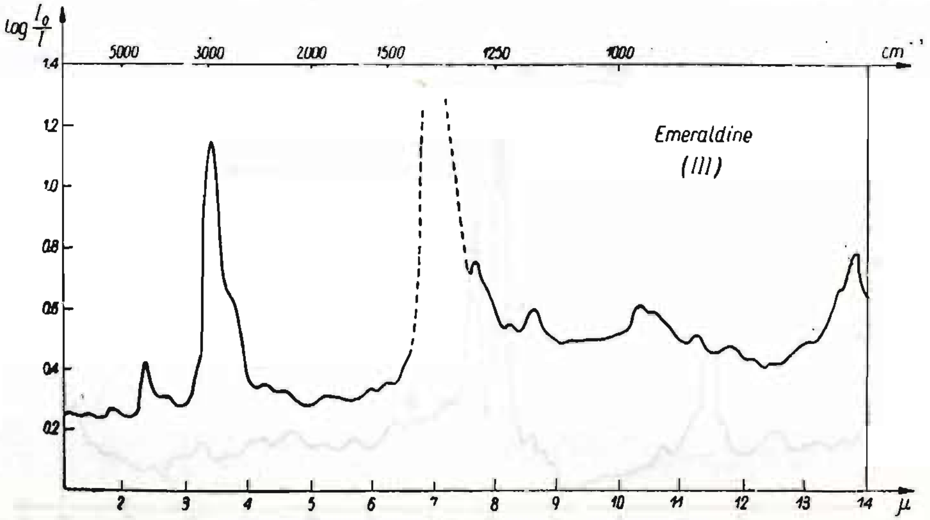

Fig. 3

The following interpretation of the absorption bands could possibly explain the similarity and differences in the structure of the compounds. (The wide and strong bands in the regions 1460—1480 cm.$^{-1}$ and 1330—1390 cm.$^{-1}$ should not be taken into consideration since they belong to the paraffin oil (vibrations of CH_2 and $C-CH_3$)).

(1) The wide and strong band between 2985 or 2940 and 2780 or 2740 or 2700 cm.$^{-1}$ should very likely be assigned to C–H aromatic stretching vibrations. It exists in the spectra of all six compounds.

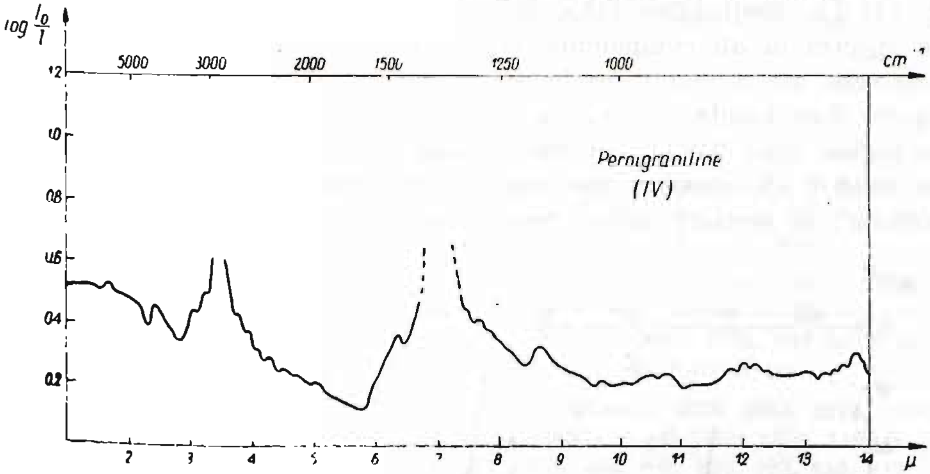

Fig. 4

(2) A weak band 1667 cm.$^{-1}$ which exists in the spectra of compounds (I)–(V) probably belongs to the vibrations of C=O groups in quinones. It does not exist in the spectrum of (VI).

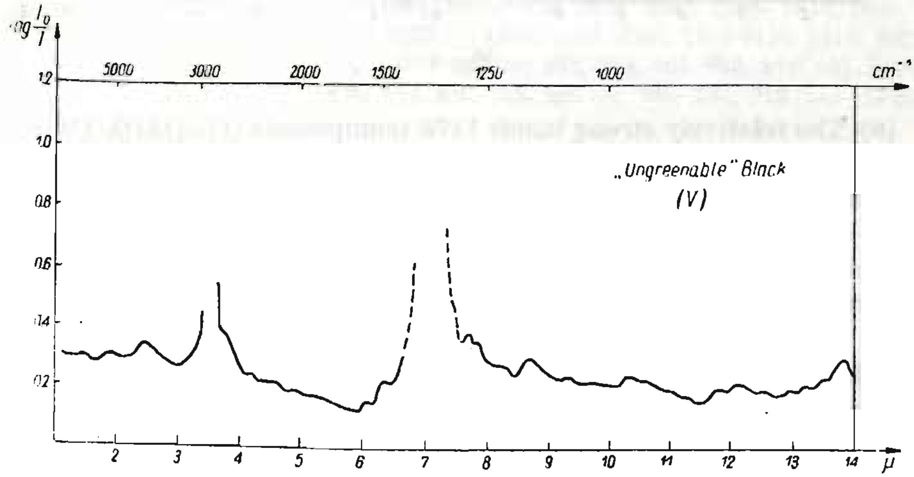

Fig. 5

The band with wave number 1613 cm.$^{-1}$ and the "shoulder" with wave number 1515 cm.$^{-1}$, which exist in the spectra of the compounds (I)–(III) should probably be ascribed to >NH deformation vibrations. They cannot be detected in the absorption curves of (IV) and (V).

This may indicate that the secondary aminogroups, which exist in anilinoquinones (I) and (II) and probably in emeraldine would disappear in the course of the oxidation of emeraldine to pernigraniline, and they are still absent in the "ungreenable" black.

(4) The frequencies 1563, 1575, 1587 and 1600 cm.$^{-1}$ which exist in the spectra of all compounds: (I), (II)—(III), (IV)—(V) and (VI), respectively, are probably produced by the conjugated aromatic rings [2].

(5) Two bands, one in the region 1333—1290 cm.$^{-1}$ and another in the region 1299—1274 cm.$^{-1}$ are probably produced by the vibrations of the bond C—N between the aromatic ring carbon and nitrogen of the secondary or tertiary amino group. They exist in all six spectra.

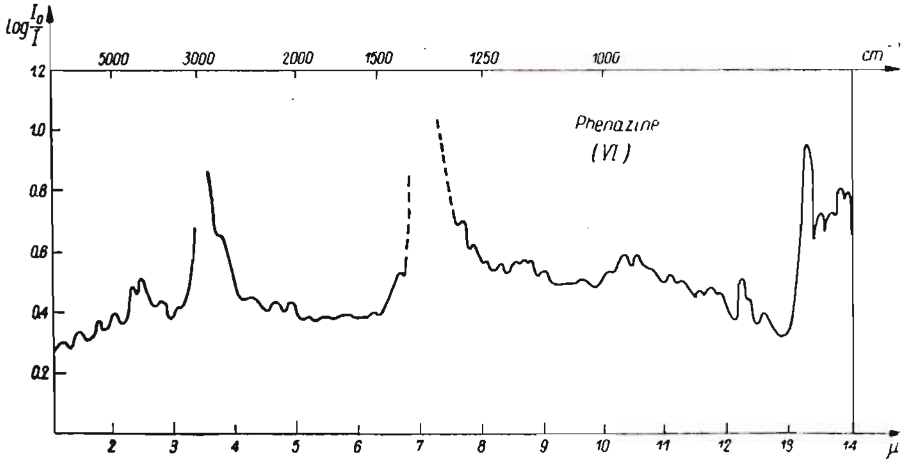

Fig. 6

(6) The relatively strong bands 1176 (compounds (I)—(III)), 1163 (IV) and 1156 cm.$^{-1}$ (V) cannot be assigned with certainty. It is not improbable that they are due to carbonyl stretching vibrations in quinones [3].

In any case they are distinctly different from the broad band (with three weak maxima) in the region 1176—1130 cm.$^{-1}$, which exists in the phenazine absorption curve (VI).

(7) The absorption spectra of the compounds (I—V) show a number of bands with frequencies near to 1000 cm.$^{-1}$. Similar bands are present in the spectrum of the compound (VI), but they slightly differ in both number and frequencies.

Thus the compounds (I)—(V) show three bands in the regions: 1087—1081 cm.$^{-1}$, 1041—1020 cm.$^{-1}$, 971—966 cm.$^{-1}$. Five bands in the same region of the spectrum of the compound (VI) are: 1111, 1075, 1036, 990, 966 cm.$^{-1}$.

They are probably produced by the vibrations of aromatic ring. It is well known that their frequencies depend on the position of substituents [2]. The frequencies of these bands suggest substitution in the positions:

1.2, 1.4, 1.2.4.,1.3 and also monosubstitution.

TABLE

No. of diagram	Substance	Absorption frequencies cm.$^{-1}$ (s) — strong, (m) — medium, (sh) — shulder
1	Anilinoquinone (I)	6667, 4167 (m), 2985-2778 (s), 2703 (sh), 2326 (m), 2151, 2000, 1667, 1613, 1563 (m),1515 (sh), 1460 (s), 1379 (s), 1316, 1290, 1227, 1176 (m), 1081 (m), 1020, 971 (m), 930, 889, 862 (m), 813, 800, 758, 743, 722 (m)
2	Dianilinoquinone (II)	5714, 4167 (m), 2985-2778 (s), 2703, 2326, 2105, 2000, 1667, 1613, 1575 (m), 1515 (sh), 1460 (s), 1379 (s), 1316, 1290, 1205, 1176 (m), 1081 (m), 1026, 966, 930, 889, 862 (m), 840 (m), 816, 758, 738, 720 (m)
3	Emeraldine (III)	5714, 4167 (m), 2985-2778 (s), 2665 (sh), 2353, 2174, 1980, 1667, 1613, 1575, 1515 (sh), 1481-1379 (s), 1316, 1282 (sh), 1212, 1176 (m), 1081, 1031, 966 (m), 930, 881 (m), 851, 826, 813, 758, 736, 720 (s)
4	Pernigraniline (IV)	6061, 4082 (m), 2985-2740 (s), 2632, 2353, 2174, 2000, 1667, 1587, 1460-1389 (s), 1333,1299, 1220, 1163 (m), 1087, 1042, 971, 930, 893, 848, 836, 823, 816, 813, 766, 752, 736, 722 (m)
5	"Ungreenable" Black (V)	5556, 4167 (m), 2985-2740 (s), 2632 (sh), 2353, 2128, 2000, 1667, 1587, 1471-1389 (s), 1307, 1274, 1212, 1156 (m), 1081, 1031, 971, 930, 889, 855, 826, 810, 775, 764, 758, 741, 720 (m)
6	Phenazine (VI)	6667, 5556, 4878, 4348, 4167 (m), 2941-2740 (s), 2667 (sh), 2353, 2273, 2174, 2041, 1905, 1835, 1600, 1481-1333 (s), 1290, 1274, 1205, 1176-1130, 1111, 1075, 1036, 990, 966 (m) 952, 939, 901, 889, 865, 851, 8440, 826, 816, 806, 796, 752 (s), 738, 727, 722 (m), 717 (m)

However, the bands do not seem to be very characteristic and cannot be taken as a proof of the anilinoquinone structure of (III), (IV) and (V). But there is great similarity between these bands in anilinoquinones (I)—(II) and in emeraldine and aniline black (II)—(V). On the contrary, the bands of phenazine (VI) differ considerably from those of (III)—(V).

(8) The bands with frequencies 862—851 cm.$^{-1}$, 816—810 cm.$^{-1}$ and intermediate frequency (e. g., 840, 826 cm.$^{-1}$) are most likely due to the aromatic C—H out of plane vibrations [3], [4]. They could not be assigned to *para* substitution, as they are also present in phenazine (VI).

(9) Two bands present in all the compounds examined, 758—752 cm.$^{-1}$ and 743—736 cm.$^{-1}$, seem to be of importance, as they would confirm that the main position of the substituents is 1.2 (in the case of all the compounds examined) and 1.2.4 (in the compound (I)—(V).

(10) The band 722—717 cm.$^{-1}$ in all compounds would suggest mono substitution. This is clear in the case of the anilinoquinones (I)—(II), where the —NH C_6H_5 group should give such a band.

Conclusion

The similarity of the infra-red absorption spectra of emaraldine, pernigraniline and "ungreenable" aniline black with the absorption spectra of anilinoquinone and dianilinoquinone seems to confirm the suggestion expressed formerly, that emeraldine, pernigraniline and "ungreenable" aniline black may possess the structure of dianilinoquinone.

Moreover, the quinoneimine structure of emeraldine and pernigraniline could not be confirmed, because of the lack of band characterising the aminogroup (3200—3400 cm.$^{-1}$) in their absorption spectra.

The phenazine structure of "ungreenable" aniline black could not be confirmed by comparison with the absorption spectrum of phenazine.

Further experiments will be carried out.

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