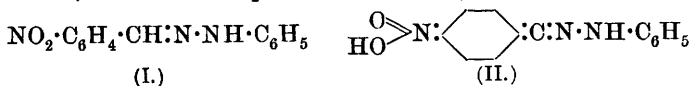


XXXIX.—*The Absorption Spectra of Nitrated Phenylhydrazones.*

By JOHN THEODORE HEWITT, RHODA MARIANNE JOHNSON, and
FRANK GEORGE POPE.

SOME few years ago Baly and Tuck (T., 1906, **89**, 982) described the absorption spectra of a number of aldehydic and ketonic phenylhydrazones, and drew attention to the colour shown by several of the nitro-derivatives. It was suggested (*loc. cit.*, p. 996) that

possibly *p*-nitrobenzaldehydephenylhydrazone does not possess the formula I, but is to be represented with a quinonoid structure (II):



Certain *p*-nitrophenylhydrazones with which we were occupied attracted our attention owing to the remarkable colour changes produced when alkalis were added to their alcoholic solutions; in fact, some of these compounds possess distinctly acidic properties. The great difference in colour between the compounds themselves and their salts led to the view that there was probably a constitutional difference.

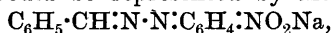
If such difference actually exists, the quinonoid formula would probably be assignable to the salt, and the conventional hydrazone formula to the hydrogen compound; although for the latter another structure is not impossible.

The most promising way of obtaining evidence of the character desired is to compare the spectra of benzaldehyde-*p*-nitrophenylhydrazone in neutral and in alkaline solution with that of *p*-nitrobenzaldehydephenylhydrazone, and, further, to examine the extent to which colour changes are inhibited by replacement of the hydrogen atoms marked with an asterisk in the formulæ:



when the solutions were rendered alkaline.

According to our view, the sodium salt of benzaldehyde-*p*-nitrophenylhydrazone would be represented by the formula:



the diminution in oscillation frequency occurring on salt formation, accompanying the greater length of chain of conjugated double linkings.

Comparison of Figs. 1 and 2 will show that, as might be expected, the *p*-nitrophenylhydrazones of benzaldehyde and of acetophenone give practically identical absorption spectra, and further, that each, when converted into a salt, shows practically the same shift in its absorption. In fact, the pairs of formulæ:



and

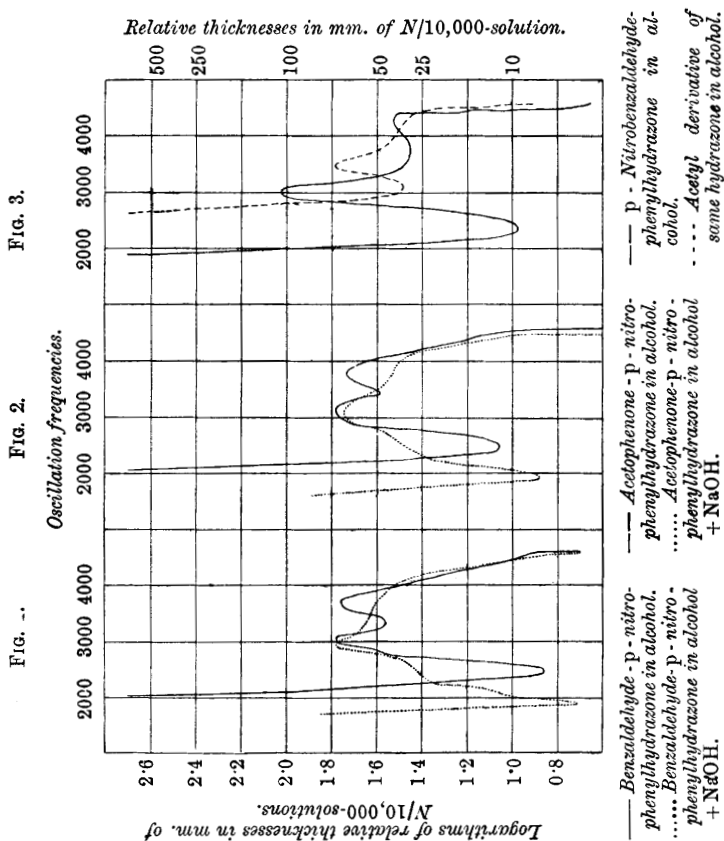


are strictly comparable.

Baly and Tuck showed that the absorption spectra of the phenylhydrazone and of the phenylmethylhydrazone of *p*-nitrobenz-

aldehyde were practically identical (*loc. cit.*, p. 996), and it is interesting to note that the head of the band in the visible spectrum lies at very much the same position as that of the band shown by the *p*-nitrophenylhydrazones of benzaldehyde and of acetophenone.

The addition of alkali hydroxides to yellow alcoholic solutions of the *p*-nitrophenylhydrazones of benzaldehyde and acetophenone causes the colour to change to red of very similar shade to magenta,

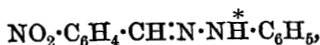


and the maximum coloration is produced by a medium amount of the alkali. In the case of the equally yellow solution of *p*-nitrobenzaldehydephenylhydrazone, as alkali is progressively added, no colour change is at first observed; a large excess produces a deepening of shade, but not a change of colour. These facts agree with our view that the compounds contain the grouping $\cdot\text{CH:N}\cdot$, for whilst the change of structure from the grouping represented by

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot$ to $\text{KNO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot$ seems to be fairly common, cases of such a change as $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot$ to $\text{KNO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot$ or $\text{KNO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot$ are comparatively rare.

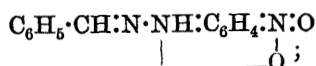
The spectrum of *p*-nitrobenzaldehydephenylhydrazone is given in Fig. 3; the curve differs slightly from that of Baly and Tuck, but the head of the band in the visible spectrum will be found at almost exactly the same persistence and oscillation frequency, namely, 2350.

Now, whilst Baly and Tuck show that both the phenylhydrazone and the phenylmethylhydrazone of *p*-nitrobenzaldehyde give virtually identical absorption spectra, it will be seen on reference to Fig. 3 that replacement of the hydrogen atom marked *

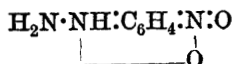


by acetyl instead of methyl shifts the absorption strongly towards the ultra-violet. One may compare this shift in the absorption with that accompanying the conversion of aniline into acetanilide.

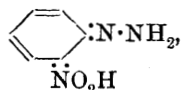
We have mentioned earlier that the hydrazones dealt with in this paper are better represented by the conventional than by quinonoid formulæ; at the same time we remarked that a different constitution was not impossible. Thus, benzaldehyde-*p*-nitrophenylhydrazone might possess an internal salt structure:



in fact, *p*-nitrophenylhydrazine itself might be:



Baly and Tuck (*loc. cit.*, p. 997) drew attention to the great difference in the absorption spectra of the *o*-nitro- and *p*-bromo-derivatives of phenylhydrazine; further than this, Borsche (*Annalen*, 1907, **357**, 171) has shown that quinones of the benzene series react with *o*-nitro- and 2:4-dinitro-phenylhydrazines with formation of hydroxyazo-compounds, whereas phenylhydrazine itself is oxidised in these circumstances. Borsche himself (*loc. cit.*, p. 173, footnote) suggests that *o*-nitrophenylhydrazine may possess the structure:



whereby this behaviour would be accounted for. The whole question as to whether many nitroamino-derivatives may not possess an internal quinonoid salt structure requires further work.

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In conclusion, we desire to express our thanks to the Research Fund Committee of the East London College for a grant defraying the costs of the investigation.

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