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THE SPECTRA OF 2,4-DINITROPHENYLHYDRAZONE ANIONS AND THE DETERMINATION OF CARBONYL COMPOUNDS IN DILUTE AQUEOUS SOLUTION

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Abstract—The spectra of 2,4-dinitrophenylhydrazones in strong alkali have been examined in the visible region, and the effect of structural variations in the ketone investigated. It is suggested that these are charge-transfer spectra, and the spectra of *o*- and *p*-nitrophenylhydrazone anions are also discussed. Standard conditions are stated so that these spectra can be used for the quantitative estimation of ketones in dilute aqueous solutions; possibilities exist for the diagnosis of the structure of such ketones.

THE presence of nitro groups in phenylhydrazones can produce colours in the visible region in alkaline conditions. Chattaway *et al.*[1] found that phenylhydrazones of nitrobenzaldehydes give colours in the visible region in alkali, and Lappin and Clark[2] found that aliphatic ketones and aldehydes give red colours with 2,4-dinitrophenylhydrazone in alkaline solution. The latter authors used this property as a basis for a method of determination of carbonyl compounds,[2] and they stated that the spectra of 2,4-dinitrophenylhydrazones in alkaline solution all had their main maximum at 480 mμ regardless of the position and number of carbonyl groups in the molecule, and that $\varepsilon_{480} = 2{\cdot}72 \times 10^4$ n, where n is the number of carbonyl groups present in the compound. During an investigation of the oxidation of alcohols and ethers,[3–5] this method was applied to the determination of small concentrations of acetone, and it was found that the main maximum of acetone 2,4-dinitrophenylhydrazone in alkaline solution is at 428 mμ, with $\epsilon_{max} = 1{\cdot}71 \times 10^4$. When the method was applied to a few simple ketones and diketones it was found that λ_{max} and ε_{max} varied with the position and number of the carbonyl groups. The author has now applied the method to other ketones and diketones, and the results confirm the variability. After the earlier oxidation work had been in progress for some time, it was discovered that Böhme and Winkler[6,7] had also found λ_{max} for the 2,4-dinitrophenylhydrazones of acetone and acetaldehyde at 428 mμ, and that Jones, *et al.*[8] had found that the main maxima for mono-carbonyl compounds in non-aqueous solvents were not at 480 mμ. The experimental work reported in this paper constitutes a complete re-investigation of the spectra of the 2,4-dinitrophenylhydrazone anions in the visible region and their use for the determination of carbonyl compounds. The spectra of similar anions from other acetone phenylhydrazones have been measured.

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[1] F. D. Chattaway, S. J. Ireland and A. J. Walker, *J. Chem. Soc.* **27**, 1851 (1925).
[2] G. R. Lappin and L. C. Clark ,*Analyt. Chem.* **23**, 541 (1951).
[3] C. F. Wells, *Nature, Lond.*, **177**, 483 (1956).
[4] C. F. Wells, *Trans. Faraday Soc.* **57**, 1703, 1719 (1961).
[5] C. F. Wells, *Disc. Faraday Soc.* **29**, 219 (1960).
[6] H. Böhme and O. Winkler, *Hoppe Seyler's Zeit. Physiol. Chem.* **296**, 274 (1954).
[7] H. Böhme and O. Winkler, *Z. Anal. Chem.* **142**, 1 (1954).
[8] L. A. Jones, J. C. Holmes and R. B. Seligman, *Analyt. Chem.* **28**, 191 (1956).

EXPERIMENTAL

Carbonyl-free methanol. MeOH was refluxed for 16 hr with 10 g of Analar 2,4-dinitrophenylhydrazine and 5 ml of Analar HCl added per l. of MeOH: 16 hr was found necessary to remove all excess HCl, which otherwise ultimately contaminated the MeOH. It was then fractionally distilled and the fraction b.p. 65° collected: the first, colourless part of the fraction could be used direct, but the rest had to be re-fractionated before use due to contamination with 2,4-dinitrophenylhydrazine.

2,4-*Dinitrophenylhydrazine reagent.* Analar 2,4-dinitrophenylhydrazine (hereafter referred to as DNP) was twice recrystallized from carbonyl-free MeOH. This purified DNP (0·100 g) were dissolved in carbonyl-free MeOH (100 ml) containing Analar HCl (0·40 ml). This can be stored for a long period in the dark: [DNP] = $5{\cdot}05 \times 10^{-3}$ M.

10% *Methanolic caustic potash.* Analar KOH pellets (40 g) were dissolved in distilled water (80 ml) in a measuring cylinder (500 ml). After cooling, this was diluted to 400 ml with carbonyl-free MeOH, and after mixing and cooling, re-adjusted to 400 ml with carbonyl-free MeOH. This was allowed to stand overnight in a closed flask and then centrifuged to remove any fine suspension of K_2CO_3 if present. The solution was stored in the dark in a stoppered bottle.

40% *Methanolic caustic potash.* This was prepared in a manner similar to that used for the 10% solution except that Analar KOH pellets (160 g) were added to the distilled water (80 ml) before diluting to 400 ml with carbonyl-free MeOH. Again, after standing overnight, the solution was centrifuged if K_2CO_3 was present, and then stored in a stoppered bottle in the dark.

Ketones and aldehydes. Pure samples of these were prepared by fractionally distilling commercially available samples (Analar where possible), except for pyruvaldehyde which was prepared by the oxidation of acetone with SeO_2,[9] and for glyoxal which was provided by Dr. D. O'Meara as a 1:1 complex with ethylene glycol. Solutions of pyruvaldehyde were standardized by treatment with H_2O_2,[10] followed by potentiometric titration of the acid produced.

Temperature control. Two temps are used for the standard conditions. For all carbonyl compounds except glycolaldehyde, 20° ± 2° is used for the formation of the hydrazones: 20° ± 2° can easily be maintained for ½ hr by placing the reaction tubes in a beaker of water. For glycolaldehyde, 75° is required to form the osazone: reaction tubes are fitted with reflux condensers and the lower portion of the tubes immersed in water in a 2 l. beaker heated by a 250 watt heater and controlled by a simmerstat unit—75° ± 1° is easily maintained in this way.

Optical density measurements. These were all done on a Unicam SP 500 spectrophotometer.

RESULTS

Spectra of 2,4-*dinitrophenylhydrazine.* The spectrum of the stock DNP solution measured against MeOH had maxima at 215, 259 and 350 mμ with extinction coefficients of $1{\cdot}25 \times 10^4$, $9{\cdot}40 \times 10^3$ and $1{\cdot}39 \times 10^4$ respectively, with a shoulder at 425 mμ where $\varepsilon = 4{\cdot}35 \times 10^3$. These can be compared with the maxima found in EtOH by Braude and Jones[11]: 219, 258, 350 and 415 mμ with $\varepsilon = 1{\cdot}20 \times 10^4$, $9{\cdot}5 \times 10^3$, $1{\cdot}45 \times 10^4$ and $6{\cdot}0 \times 10^3$ respectively. Differences in the region 415–425 mμ might be due to differences in minute amounts of carbonyl impurity in the solvent.

In 5% KOH in 75% v/v MeOH $5{\cdot}05 \times 10^{-5}$ M DNP gives maxima at 226, 273 and 328 mμ with $\varepsilon = 1{\cdot}14 \times 10^4$, $1{\cdot}23 \times 10^4$ and $2{\cdot}61 \times 10^3$ respectively: at 428 mμ, $\varepsilon = 1{\cdot}49 \times 10^3$. However, it was found that DNP itself in alkaline solution does not obey Beer's Law: $5{\cdot}05 \times 10^{-4}$ M DNP in 5% KOH in 78% v/v MeOH gives at 328 mμ $\varepsilon = 1{\cdot}32 \times 10^3$, and at 428 mμ $\varepsilon = 8{\cdot}3 \times 10^2$.

The formation of acetone 2,4-*dinitrophenylhydrazone.* Lappin and Clark's procedure[8] consisted of adding a solution of the carbonyl compound (1 ml) to a saturated solution of DNP (1 ml) in carbonyl-free MeOH containing HCl and heating for 30 min at 50° or 5 min at 100°: the colour was developed by adding 10% methanolic KOH (5 ml) and measured directly at 480 mμ. In the experience of the present author this procedure gave irreproducible results. Moreover, it was found that the hydrazone could be formed readily at room temp, and Böhme and Winkler[6,7] also found this.

The following procedure was found to be satisfactory, and adopted as the standard method. An aqueous solution of the carbonyl compound (2 ml) in a suitable concentration were pipetted into the standard DNP solution (2 ml) contained in a calibrated tube: this tube consisted of a B14 Quickfit

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[9] H. L. Riley, J. E. Morley and N. A. C. Friend, *J. Chem. Soc.* 1875 (1932),

[10] T. E. Friedemann, *J. Biol. Chem.* 73, 331 (1927).

[11] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.* 489, (1945).

socket with a wider portion added at the bottom and calibrated for 20 ml on the narrow portion. The carbonyl solution (2 ml) were pipetted on to the wall of the tube just above the level of the DNP solution (pipetting on to the surface of the DNP solution leads to irreproducible results), and the solution was mixed by swirling in the bottom of the tube, ensuring that any splashes on the higher portion of the tube were washed into the bulk by manipulation of the 4 ml: A blank mixture of DNP solution (2 ml) and distilled water (2 ml) was prepared in a similar manner in a similar tube. Such mixtures were left for ½ hr at ~20° to allow the hydrazone to form, and then the 10% methanolic KOH reagent (10 ml) were added to each tube. After thorough shaking, the solution in each tube was diluted to the 20 ml mark with carbonyl-free MeOH. The concentration of MeOH is now 78% v/v. After thorough shaking again, the spectrum of the red anion was measured against the blank: in 5% KOH in 78% v/v MeOH the anion has maxima at 286, 428 and 530 mμ with extinction coefficients of $2{\cdot}60 \times 10^3$, $1{\cdot}71 \times 10^4$ and $9{\cdot}8 \times 10^3$ respectively (Fig. 1).

Table 1 shows that ½ hr at 20° ± 2° is sufficient for maximum formation, and this applies over the whole range possible using 1 cm and 4 cm cells. Figure 1 shows that variation in the MeOH concentration has no detectable effect on λ_{max}, and the effect on ε_{max} is shown in Table 2: a final concentration of 78% v/v was used in the standard procedure. Table 3 shows that maximum formation occurs in the 1·25 M (or 5%) KOH. Fading of the red colour was found to be negligible in the 15 min after development (Table 4). Using the standard conditions for formation of the hydrazone and development of the red colour, Beer's Law was found to be obeyed at 428 mμ for final concentrations of the red anion between $6{\cdot}8 \times 10^{-6}$ M and $1{\cdot}2 \times 10^{-4}$ M.

Other mono-ketones. The above standard procedure was applied to other mono-ketones, and Beer's Law was found to be obeyed over the 1·0 and 0·1 scales of the Unicam SP 500 using 1 cm and 4 cm cells. The spectra are shown in Fig. 2: all aliphatic ketones have maxima identical with those quoted above for acetone. Spectral details are listed in Table 6.

TABLES 1–4. ACETONE 2,4-DINITROPHENYLHYDRAZONE: VARIATION OF OPTICAL DENSITY AT 428 mμ IN 1 cm CELLS D_{428}; [ACETONE] = $3{\cdot}40 \times 10^{-5}$ M

TABLE 1		TABLE 2		TABLE 3		TABLE 4	
Time (min)	D_{428}	[Methanol] % v/v	D_{428}	[KOH]M	D_{428}	Time after mixing (min)	D_{428}
5	0·407	10	0·456	0·63	0·445	0	0·570
10	0·422	47·5	0·535	1·25	0·560	20	0·555
20	0·532	78	0·580	2·50	0·579	45	0·535
30	0·570	80	0·625				
50	0·585	87·5	0·670				
75	0·575						

TABLE 5. ACETALDEHYDE 2,4-DINITROPHENYLHYDRAZONE ANION: VARIATION OF OPTICAL DENSITY AT 428 mμ IN 1 cm CELLS, D_{428}, WITH TIME OF FORMATION; [ACETALDEHYDE] = $5{\cdot}44 \times 10^{-6}$ M

Time of formation (min)	D_{428}
15	0·830
30	0·900
45	0·860
60	0·845

Aldehydes. Using the standard conditions for ketones, the spectra of the 2,4-dinitrophenylhydrazone anions in alkaline solutions from acetaldehyde and formaldehyde had maxima at 428 mμ, but the colour faded rapidly. In contrast, Lappin and Clark[3] stated that the main maximum in the visible region appeared at 480 mμ and that the intensity of the colour at the maximum was stable in 5% KOH: however, Böhme and Winkler[6] also found the maximum at 428 mμ for acetaldehyde and observed the instability of the coloured anion in their experiments. It was found that the colour with acetaldehyde could be stabilized by using more concentrated solutions of KOH: in 20% KOH solution (obtained by adding 10 ml of the 40% reagent) the fading at 428 mμ was reduced to 2% in 10 min. Table 5 shows that full formation of acetaldehyde 2,4-dinitrophenylhydrazone takes place in ½ hr at 20°. Beer's Law was obeyed for acetaldehyde in 20% KOH; details of extinction coefficients are given in Fig. 2 and Table 6. Böhme and Winkler[8] found that the colour could be stabilized by the addition of pyridine to the 5% KOH, presumably due to the increase in the total basicity of the solution as with the increased concentration of KOH.

Di-carbonyl compounds. The spectra of the 2,4-dinitrophenylhydrazone anions are shown in Figs. 1 and 3 and values for ε_{max} given in Table 6. The anion for acetylacetone required about 15 min after addition of KOH and MeOH to the 4 ml formation mixture for the colour to achieve its maximum intensity.

The glyoxal used originated as a 1:1 complex with ethylene glycol, and experiments adding ethylene glycol showed that this had no effect on λ_{max} or ε_{max}. Maximum formation of the osazone occurred in the usual way in ½ hr at 20°. However, after the addition of the 10% KOH (10 ml) the solutions had to be diluted to 20 ml with distilled water to avoid precipitation in the final alkaline solution. Beer's Law is obeyed over the whole range over which the blue ion can be measured i.e. final concentrations of blue ion from $2{\cdot}5 \times 10^{-7}$ M to $1{\cdot}5 \times 10^{-5}$ M. Above a concentration of $1{\cdot}5 \times 10^{-5}$ M, fading of the blue ion is too rapid for accurate measurement, and Beer's Law is no longer obeyed.

Glycolaldehyde. Under the standard conditions of hydrazone formation (0·025 M HCl for ½ hr at 20°), only the red colour of the anion of a mono-carbonyl compound develops on addition of 10% KOH. Increasing the acid concentration had no further effect in ½ hr at 20°, but when more concentrated solutions of DNP and glycolaldehyde were allowed to stand for 48 hr at room temp, a precipitate appeared, which gave a blue colour with alkali and micro-analysis showed to be bis-2,4-dinitrophenylhydrazone of glyoxal, indicating, as expected, that the DNP had oxidized the >CHOH group. By varying the temp, the acid concentration and the time of formation for aqueous glycolaldehyde (2 ml) and DNP (2 ml) the following conditions were found for optimum formation of the osazone: 50 min in 1·5 M HCl at 75°. The reaction tubes are fitted with reflux condensers when in the water bath at 75°; after 50 min the condensers are washed down with carbonyl-free MeOH into the reaction tubes, and the colour developed by the addition of 10% KOH; as with glyoxal, the solutions are diluted to 20 ml with distilled water to avoid precipitation. Beer's Law was obeyed over the range of final concentrations of blue ion between $2{\cdot}5 \times 10^{-7}$ M to $1{\cdot}5 \times 10^{-5}$ M using 1 cm and 4 cm cells: ε_{max} is $5{\cdot}24 \times 10^4$. Similar strictions about the rate of fading apply as stated for glyoxal.

DISCUSSION

The results in Table 6 do not support the claim of Lappin and Clark[2] that λ_{max} is always at 480 mμ with $\varepsilon_{max} = 2{\cdot}72 \times 10^4 n$ (n = no. of carbonyl groups). The contention of Lappin and Clark has been widely reported in the analytical literature.[12–16] Table 6 indicates that for aliphatic mono-carbonyl compounds $\lambda_{max} =$ 428 mμ independent of alkylation: all have a subsidiary maximum in the visible region at 530 mμ. Attachment of phenyl groups to the mono-carbonyl carbon atom causes an increasing bathochromic shift. For α-dicarbonyl compounds only one peak is found with $\varepsilon_{max} > \varepsilon_{max}$ for the mono-carbonyl compounds: increasing alkylation produces a blue shift in λ_{max}. For the β-dicarbonyl compound, acetylacetone, λ_{max} is at longer wavelengths than for mono-carbonyl compounds, but for the γ-dicarbonyl compound, hexane-2,5-dione, λ_{max} is moved to shorter wavelength.

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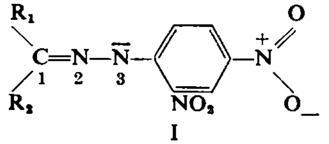
[16] N. D. Cheronis and T. S. Ma, *Organic Functional Group Analysis* p. 145. Interscience, New York (1964).

TABLE 6

Carbonyl compound	λ_{max} (mμ)	ε_{max} (mμ)	Subsidiary λ_{max} (mμ)
Acetone	428	$1{\cdot}71 \times 10^4$	530
Methyl ethyl ketone	428	$1{\cdot}46 \times 10^4$	530
Methyl n-propyl ketone	428	$1{\cdot}56 \times 10^4$	530
Cyclohexanone	428	$1{\cdot}65 \times 10^4$	530
Cyclopentanone	428	$1{\cdot}38 \times 10^4$	530
Acetaldehyde	428	$1{\cdot}65 \times 10^4$	545
Glyoxal	580	$5{\cdot}90 \times 10^4$	—
Pyruvaldehyde	555	$4{\cdot}48 \times 10^4$	—
Diacetyl	502	$3{\cdot}67 \times 10^4$	—
Acetyl acetone	450	$3{\cdot}33 \times 10^3$	flat 490–520
Hexane-2,5-dione	418	$2{\cdot}02 \times 10^4$	530
Acetophenone	450	$1{\cdot}50 \times 10^4$	shoulder 530–540
Benzophenone	464	$6{\cdot}14 \times 10^3$	shoulder 550

These spectra in the visible region in alkaline solution must arise from electronic changes in the anion formed by loss of a proton from nitrogen atom No. 3 (I). Electronic transitions responsible for the light absorption could be of the n–π^*, π–π^*, or charge-transfer type. At first sight, it might be concluded that this is a classic case of an n–π^* transition: protonation produces a blue shift (428 mμ to 328 mμ), which is regarded as diagonistic of an n–π^* transition.[17,18] The localized negative charge from the non-bonded electrons on nitrogen 3 would be transferred to an anti-bonding molecular orbital involving atoms 1,2 and 3, the benzene ring and the nitro-groups (I).



I

However, owing to the high values of ε_{max}, possibly this is one case where the blue shift on protonation[17,18] is not diagnostic of a simple n–π^* transition, as n–π^* transitions in azo-compounds lead to much lower values for extinction coefficients[19,20] i.e. $\varepsilon \sim 450$–1500. Two other possibilities exist. Overlap of the p orbital on nitrogen 3 with p orbitals on atoms 1 and 2, the benzene ring and the nitro groups provides a system in which π–π^* transitions are possible. The peaks in the near UV in nitrobenzenes have been interpreted[21–24] in terms of charge transfer from the benzene ring to the nitro group, and such an electronic shift will be encouraged[25,26] by an electron-donating site such as the charge on nitrogen 3 i.e. the charge-transfer band will move to longer wavelengths. Thus the ground state π orbital must retain some localization

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of the negative charge on nitrogen 3, and more is transferred towards the nitro-groups on excitation. The insensitivity of λ_{max} and ε_{max} of the aliphatic mono-carbonyl compounds to an increasing electron-repelling inductive effect at carbon 1 by alkylation at R_1 and R_2 (Table 6 and Fig. 1 and 2) suggests that electronic shifts on excitation must be at the other end of the molecule,[27a] and supports a shift of charge from nitrogen atom 3 through the benzene ring to the nitro-groups. However, carbon 1 and nitrogen 2 will still be involved by π overlap, probably in both the ground and excited states: the bathochromic shift in λ_{max} from 428 mμ to 450 mμ with little change in ε_{max} when R_1 = phenyl and $R_2 = CH_3$ is consistent with the effect of lengthening the π orbital system[27b] by overlap on the phenyl group. Moreover, when $R_1 = R_2$ = phenyl, a further bathochromic shift occurs, but ε_{max} is considerably reduced. Increasing the extent of π overlap on the additional phenyl group is again probably responsible for the further red shift, but the decrease in ε_{max} suggests that the overlap between the π orbitals of the phenyl groups and that of the carbon-nitrogen system is weak. This weak overlap is not apparent when only R_1 = phenyl, suggesting that, due to the angle between the sp^2 bonds of carbon 1, the co-planarity of the two phenyl groups necessary for maximum overlap is sterically hindered. For such steric effects in conjugated systems it has been shown[28,29] that ε and ε_0, the extinction coefficients for the strained and non-strained structure respectively, and the angle of twist ϕ are related by $\varepsilon/\varepsilon_0 = \cos^2 \phi$, and this has also been applied to the charge-transfer spectra of substituted nitrobenzenes.[30] From this relationship and the values

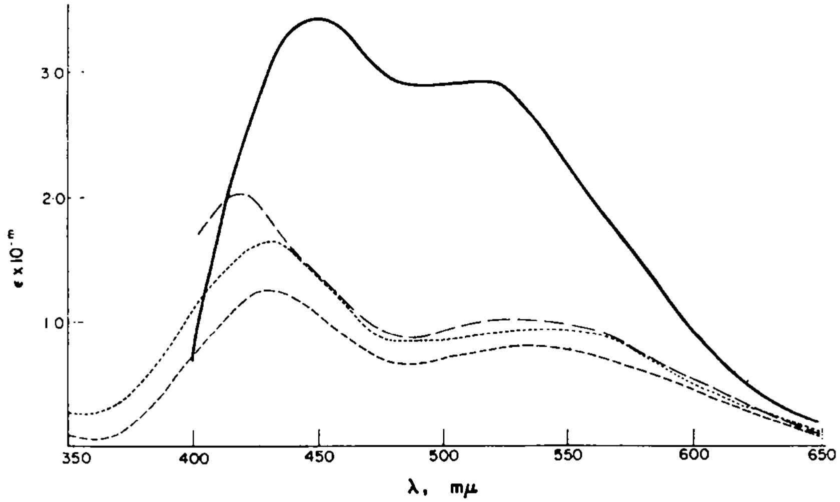

FIG. 1. Spectra of 2,4-dinitrophenylhydrazone anions (ε = molar extinction coefficient):
———— acetylacetone, m = 3;
— — —, hexane-2,5-dione, m = 4;
· · · · · · · ·, acetone in 78% methanol, m = 4;
- - - - - - -, acetone in 10% methanol, m = 4.

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[27] J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules* [a] Chap. 9, [b] Chap. 5. Methuen, London (1963).

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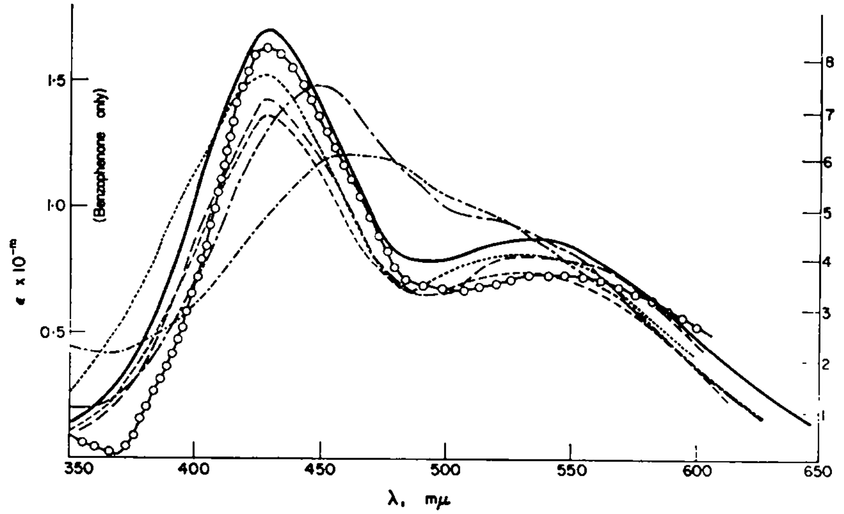
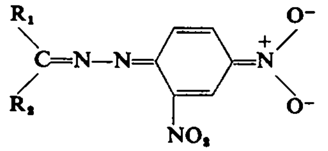


FIG. 2. Spectra of 2,4-dinitrophenylhydrazone anions (ε = molar extinction coefficient):

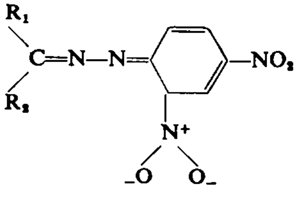
————, cyclohexanone, m = 4;
— — — — —, methyl ethyl ketone, m = 4;
···········, methyl n-propyl ketone, m = 4;
- - - - - - - -, cyclopentanone, m = 4;
—O—O—C—, acetaldehyde, m = 4;
— · — · — · —, acetophenone, m = 4;
- · - · - · - · -, benzophenone, m = 2.

of ε_{max} for acetone and benzophenone, the angle between the planes of the benzene rings in the latter anion is found to be 79°.

All the mono-carbonyl 2,4-dinitrophenylhydrazone anions show two maxima in the visible region. On valence-bond theory, such a charge-transfer would be interpreted as involving transfer from a structure of type I to a resonance hybrid of two quinone-diimine systems II and III[3] i.e. one peak only would be expected. However, it has been suggested that the application of resonance theory to such charge-transfers is not valid.[23,24] On molecular orbital theory, the two peaks of the mono-carbonyl



II



III

anions can be ascribed to two charge-transfer states, one to each nitro group. This view is supported by the spectra of the acetone mono-nitrophenylhydrazone anions.

Figure 3 shows that anions derived from *o*- and *p*-nitrophenylhydrazones have only one peak in the visible region derived from one charge-transfer state involving the nitro group: no absorbance in the visible region was obtained for the *m*-nitrophenylhydrazone or the phenylhydrazone in this concentration range.

Table 2 shows that $\varepsilon_{\max}$ for acetone 2,4-dinitrophenylhydrazone anion changes with solvent composition, decreasing with increasing water content, although Fig. 1 shows that there is no change in $\lambda_{\max}$. This is not likely to be a dielectric effect, as the net result of the charge-transfer is the transfer of the negative charge on nitrogen 3 elsewhere in the molecule. More likely this decrease in $\varepsilon_{\max}$ without change in $\lambda_{\max}$ results from localized hydration restricting π overlap by hindering co-planarity.

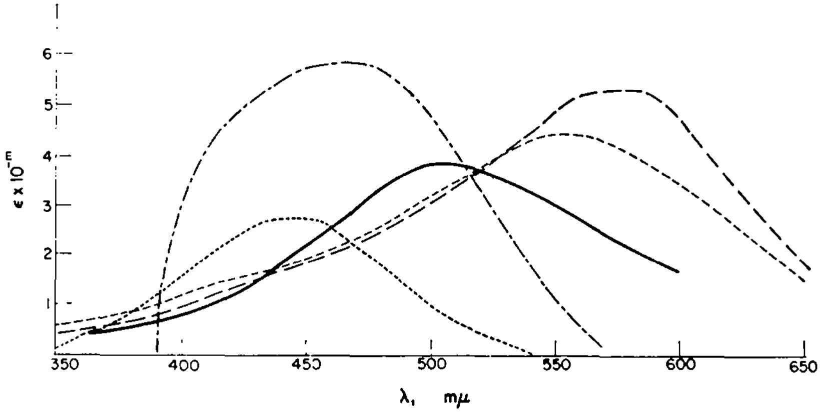
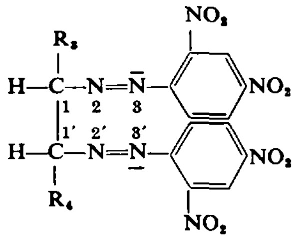


Fig. 3. Spectra of 2,4-dinitrophenylhydrazone anions:
————, diacetyl, m = 4;
— — — —, glyoxal, m = 4;
- - - - - - - -, pyruvaldehyde, m = 4.
Spectra of acetone mono-nitrophenylhydrazone anions:
—·—·—, *p*-nitro, m = 3;
·· ········, *o*-nitro, m = 3.

Figure 3 shows that the anions derived from the α-dicarbonyl compounds have only one peak. However, $\varepsilon_{\max}$ is greater than for the mono-carbonyl compounds, and possibly this indicates that two charge-transfer states are superimposed in the spectra. Presumably π overlap occurs between carbon atoms 1 and 1′ (IV), extending over both dinitrophenylhydrazine groups. This is confirmed by the effect of increasing alkylation at R_3 and R_4: an increase in the electron-releasing inductive effect causes



IV

a hypsochromic shift in $\lambda_{\max}$ (Table 6 and Fig. 3), suggesting that the electron density at carbons 1 and 1′ is increased on excitation.

The spectrum for the anion derived from acetylacetone (Fig. 1) is similar to that for acetone with a bathochromic shift in λ_{max} and a much lower value for ε_{max}. The shift in λ_{max} suggests that some π overlap occurs across the ionized methylene group, but the lower ε_{max} indicates that the overlap is only weak. Possibly some freedom of rotation still exists in the C—C bonds from the methylene carbon. The slow development of colour in this case may be due to a slow change of the methylene carbon from sp^3 to the $sp^2 + p$ arrangement. The spectrum for the anion from hexane-2,5-dione is similar to that for acetone (Fig. 1) with ε_{max} of the same order but a small blue shift in λ_{max}. Possibly the latter shift is caused by some mutual steric hindrance by the dinitrophenylhydrazine groups.

An analytical method for carbonyl compounds. As Beer's Law is obeyed at λ_{max} or all the 2,4-dinitrophenylhydrazones in Table 6, this data can be used for the determination of these carbonyl compounds with the standard experimental procedure as described for acetone apart from glycolaldehyde which requires a higher temperature and acetaldehyde which requires the addition of 40% KOH for stability. The method has been used for the determination of carbonyl products from the oxidation of alcohols by photo-excited quinones,[3–5] phenyl radicals[31] and transition metal cations,[32] and from the γ-radiolysis of DL-madelic acid and pentane-1,5-diol,[33] and for the determination of the acetone content of cellulosic films.[34] Possibilities for the characterization of carbonyl products exist with the variation of λ_{max} with structure and the lability of the aldehyde anions in 10% alkali.

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[32] C. F. Wells and G. Davies, unpublished results.
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[34] R. Jeffries, *J. Textile Inst.* **49**, T192 (1958).