128. *Studies in Light Absorption. Part II. 2 : 4-Dinitrophenylhydrazones.*

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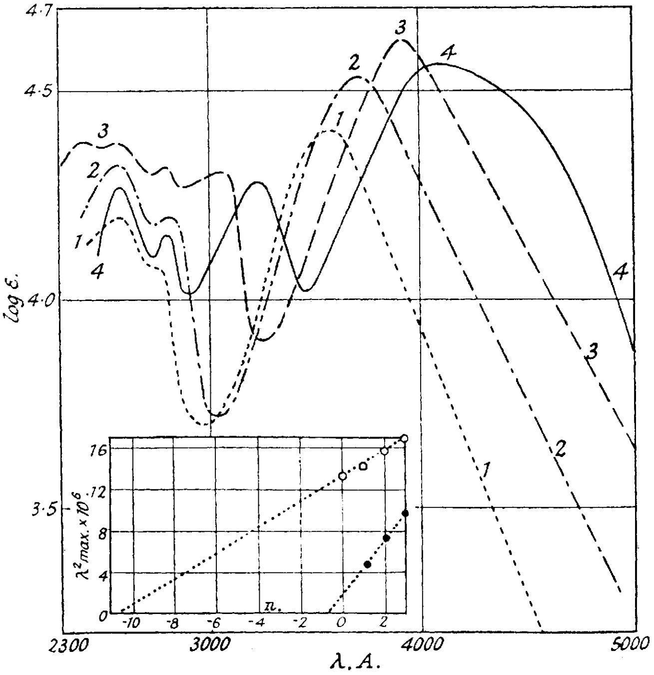
The visible and the ultra-violet light absorption properties of some fifty dinitrophenylhydrazones have been determined in both alcoholic and chloroformic solution. These properties are dependent upon the extent of the conjugated unsaturation present in the parent carbonyl compound, and alkyl substitution effects have also been observed (see Table II). The classified data provide structural evidence useful in degradative work and are of considerable theoretical interest in connection with the optical properties of the >C:N– and the >NH group.

Extensive data are already available regarding the light absorption of several classes of carbonyl derivative, particularly the semicarbazones, phenylsemicarbazones, thiosemicarbazones, and oximes (Burawoy, J., 1941, 20; Evans and Gillam, J., 1943, 565). The derivatives most widely used at present, however, for the characterisation of carbonyl compounds are the 2 : 4-dinitrophenylhydrazones, first introduced by Brady (*Analyst*, **1926**, **51**, 77). A comprehensive collection of light-absorption data for these compounds appeared desirable for purely practical purposes, since preliminary studies had shown that the wave-length position of the main maximum in the extinction curve varied significantly with the degree of conjugated unsaturation of the parent carbonyl compound (Jones, Wilkinson, and Kerlogue, J., 1942, 735). It was subsequently found that the correlation between structure and light absorption in this series is much closer than was anticipated, and is of considerable theoretical interest with regard to the optical properties of the >C:N– and >NR groups.

Fig. 1.



1. *Acetaldehyde.* 2. *Crotonaldehyde.* 3. 3-*Methylsorbaldehyde.* 4. *Octatrienal.*

○ = $(C:C)_n$·C:N·NHX. ● = $(C:C)_n$·CHO.

Light absorption of 2 : 4-*dinitrophenylhydrazones in chloroform solution.*

In degradative work leading to aldehydic or ketonic products, it is often possible to isolate sufficient quantities of the water-insoluble dinitrophenylhydrazones for spectrographic examination when the isolation of the carbonyl compound itself is impracticable. The colour of the crystalline derivative provides a rough but not absolutely reliable indication of the degree of unsaturation of the parent compound, usually varying from yellow in the case of saturated aldehydes and ketones to dark red in the case of the triply unsaturated aldehyde octatrienal. Very much more precise information can now be obtained from a comparison of the light-absorption curve with the data given in Table II.

Data for the light-absorption maxima of some fifty 2 : 4-dinitrophenylhydrazones in the 2200—5000 A. range are collected in Table I. As far as possible solutions in both alcohol and chloroform were examined within the limitations imposed by solubility and availability of material. With chloroform solutions the extinction curves cannot be followed below 2300A. because of the absorption of the solvent. Principal (long wave-length) bands are given in heavy type and are summarised in Table II.

TABLE I.

Light absorption of 2 : 4-*dinitrophenylhydrazones.*

Carbonyl compound.*	Solvent : EtOH.†		Solvent : CHCl$_3$.†	
	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.
H·CHO (166°)	2250	185	2580	120
	2560	120	2800	80
	3480	**230**	**3480**	**230**
Me·CHO (167°)	2280	170	2570	155
	2560	140	2790	105
	3600	**215**	**3600**	**250**
Et·CHO (156°)	2280	160	2520	140
	2560	130	2800	120
	2780	90	**3610**	**210**
	3570	**215**		
Pr^a·CHO (107°)	2230	160	2580	130
	2560	125	**3580**	**220**
	3560	**220**		
n-C$_6$H$_{13}$·CHO (107°)	2280	145	2560	135
	2560	110	2790	80
	2800	75	**3580**	**200**
	3560	**205**		
COMe$_2$ (128°)	2280	185	2580	125
	2550	135	2790	105
	3620	**215**	**3660**	**225**
COMeEt (115°)	2280	200	2580	115
	2550	145	2800	75
	3620	**230**	**3650**	**220**
COMePr^a (145°)	2280	210	2600	115
	2550	155	2800	95
	2800	80	**3680**	**225**
	3620	**250**		
COMeBu (*n*) (108°)	2280	180	2560	100
	2560	95	2790	70
	2810	40	**3650**	**195**
	3620	**175**		
COEt$_2$ (155°)	2290	190	2550	165
	2510	135	2790	125
	2780	85	**3660**	**250**
	3620	**220**		
COMe·CH$_2$·CH$_2$·CH:CMe$_2$ (125°)	2280	160	2570	135
	2560	105	2800	115
	2800	75	**3670**	**210**
	3650	**205**		
COMe·CH$_2$·CH$_2$·CO$_2$H (205°)	—	—	2620	125
			2780	70
			3650	**230**
H·CO·CH$_2$·CO$_2$H (150°) [1]	2280	130	2560	110
	2560	115	**3510**	**195**
	3500	**200**		
COMe·CH$_2$·CO$_2$H (125°) [1]	2280	175	2560	110
	2560	105	**3600**	**205**
	3580	**205**		
*cyclo*Pentanone (146°)	2280	170	2580	125
	2550	140	2790	90
	2800	80	**3670**	**245**
	3630	**225**		
*cyclo*Hexanone (162°)	2280	170	2550	130
	2550	145	2800	95
	2800	80	**3660**	**245**
	3630	**235**		
Menthone (144°)	—	—	2600	185
			2790	125
			3650	**255**
Ketone (293°) [2]	—	—	2420	200
			2580	180
			2810	140
			3680	**240**
Sitostanone (209°) [3]	—	—	2550	180
			2810	140
			2910	100
			3680	**255**
Ph·CH(OH)·COMe (174°)	2280	145	2560	150
	2560	155	2810	115
	3670	**240**	**3700**	**220**

* M. p.'s of dinitrophenylhydrazones given in parentheses.

† Principal bands in heavy type.

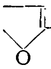
TABLE I (contd.).

Light absorption of 2 : 4-dinitrophenylhydrazones.

Carbonyl compound.	Solvent : EtOH.		Solvent : $CHCl_3$.	
	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.
COMe·CO_2H (219°)	2420	105	2420	120
	2560	105	2560	120
	3550	**225**	**3600**	**225**
COEt·CO_2H (191°) [1]	2280	120	2420	125
	2430	125	2520	125
	2520	125	**3650**	**255**
	3640	**235**		
COPr$^{\beta}$·CO_2H (194°) [1]	2280	130	2450	180
	2430	130	2510	180
	2520	130	**3660**	**250**
	3660	**240**		
COMe·COPr$^{\alpha}$ (107°)	2290	135	2560	130
	2560	115	2800	115
	3510	**245**	**3520**	**260**
COMe·CH_2·CH_2·COMe (bis) (257°)	—	—	2570	200
			3660	**230**
COMe·COEt (bis) (280°)	—	—	2560	230
			4000	**440**
			4400	365
CH_2:CH·CHO (166°)	2280	150	2560	105
	2410	150	2820	80
	2510	150	**3670**	**260**
	2810	95		
	3660	**255**		
CHMe:CH·CHO (190°)	2440	180	2560	180
	2560	180	2810	135
	2800	120	**3720**	**290**
	3730	**285**		
CMe_2:CH·CHO (179°)	2560	185	2600	200
	2810	115	2960	155
	3810	**285**	**3820**	**240**
CHPr:CEt·CHO (123°)	2560	210	2570	170
	2800	160	2810	120
	3780	**305**	2920	85
			3850	**270**
Citral (–CMe:CH·CHO) (125°)	2450	200	2570	235
	2560	200	2800	180
	2800	185	2910	155
	2910	115	**3850**	**310**
	3830	**300**		
Unsaturated aldehyde (–CH:CMe·CHO) (149°) [4]	2280	195	2560	215
	2550	195	2820	165
	2870	120	2920	140
	2910	105	**3830**	**305**
	3770	**280**		
Unsaturated aldehyde (–CH:CMe·CHO) (165°) [4]	2440	175	2560	190
	2530	175	2810	145
	2810	135	2900	110
	2910	120	**3830**	**295**
	3810	**320**		
β-*cyclo*Citral (–CMe:$\overset{\vert}{C}$·CHO) (173°)	2250	140	2570	175
	2550	155	2790	150
	2820	100	2920	115
	3870	**265**	**3890**	**280**
Ph·CHO	2230	245	2550	150
	2530	130	**3770**	**285**
	3770	**295**		
CMe_2:CH·COMe (200°)	2240	165	2550	190
	2560	175	2800	140
	2800	100	2910	100
	3790	**225**	**3890**	**250**
α-Ionone (–CH:CH·COMe) (138°)	2230	170	2560	225
	2450	185	2800	185
	2520	185	2900	170
	2820	145	**3890**	**250**
	3770	**280**		
Acetyl-Δ^1-*cyclo*hexene (>C:$\overset{\vert}{C}$·COMe) (207°)	2280	155	2530	200
	2550	155	2810	165
	2800	130	**3870**	**275**
	3770	**240**		

TABLE I (contd.).

Light absorption of 2 : 4-*dinitrophenylhydrazones.*

	Solvent : EtOH.		Solvent : $CHCl_3$.	
Carbonyl compound.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$
Δ^4-Cholestenone (>C:CH·CO–) (233°) [3]	—	—	2560	215
			2810	160
			2920	115
			3930	**295**
Δ^4-Sitostenone (>C:CH·CO–) (247°) [3]	—	—	2590	215
			2820	160
			2920	140
			3950	**315**
Stigmastadienone (>C:CH·CO–) (245°) [3]	—	—	2420	215
			2650	230
			2800	185
			2930	170
			3930	**310**
COPhMe (249°)	2180	275	2560	140
	2650	200	2800	120
	2800	190	2900	105
	3770	**260**	**3800**	**275**
COPh·CH(OH)Ph (174°)	—	—	2580	210
			2800	160
			3910	**300**
CHMe:CMe·CH:CH·CHO (194°) [5]	—	—	2420	235
			2600	235
			2800	210
			3080	185
			3920	**420**
CMe_2:CH·CH_2·CH_2·CMe:CH·CH:CH·CHO (132°) [6]	—	—	2650	460
			3080	370
			4000	**460**
Furfuraldehyde (223°)	2270	150	2580	180
	2560	125	2780	120
	2800	85	3020	105
	3000	85	**3880**	**265**
	3900	**270**		
ψ-Ionone (–CMe:CH·CH:CH·COMe) (140°)	2280	170	2570	220
	2600	150	2790	200
	2810	135	3090	220
	3070	185	**4070**	**345**
	3950	**320**		
β-Ionone (–CMe:$\overset{\mid}{\mathrm{C}}$·CH:CH·COMe) (126°)	2290	155	2560	205
	2500	165	2820	165
	2800	120	2920	145
	3850	**265**	**3880**	**275**
Ketone (–CH:$\overset{\mid}{\mathrm{C}}$·$\overset{\mid}{\mathrm{C}}$:CH·CO–) (228°) [7]	—	—	2580	250
			2800	200
			3070	150
			4000	**335**
CMe_2:CH·CO·CH:CMe_2 (108°)	2260	200	2560	135
	2580	160	2810	70
	2800	110	**3950**	**245**
	3880	**245**		
$COPh_2$ (238°)	2430	180	2420	205
	3790	**265**	**3910**	**290**
CHMe:CH·CH:CH·CH:CH·CHO (203°)	2280	210	2580	190
	2560	210	2800	145
	2800	180	3250	190
	3130	235	**4100**	**365**
	4090	**480**		
—CH:CMe·COEt (188°) [7]	2300	200	2570	265
	2450	200	2800	240
	2510	200	3080	265
	3100	220	**4000**	**425**
	3160	210		
	3960	**435**		

References to origin: [1] Owen, J., 1945, in the press. [2] Jones and Koch, J., 1942, 393. [3] Jones, Wilkinson, and Kerlogue, J., 1942, 391. Heilbron, Johnson, Jones, and Spinks, J., 1942, 727. [5] Heilbron, Jones, and Koch, J., 1942, 735. [6] Kuhn, Badstübner, and Grundmann, *Ber.*, 1936, **69**, 105. [7] Heilbron, Johnson, and Jones, J., 1939, 1560.

TABLE II.

Principal bands of 2 : 4-dinitrophenylhydrazones and corresponding carbonyl compounds.

System.	$\lambda_{max.}$ (EtOH), A.	$\lambda_{max.}$ ($CHCl_3$), A.	$\varepsilon_{max.} \times 10^{-2}$.	System.	$\lambda_{max.}$ (EtOH), A.	$\varepsilon_{max.} \times 10^{-2}$.	$\Delta\lambda$.*	$\Delta\varepsilon$.
$NHX\cdot NH_2$	3500	3430	150					
$NHX\cdot N{:}CH_2$	3480	3480	200—300	$O{:}CH_2$	No high intensity absorption $>\lambda = 2000$ A.			
$NHX\cdot N{:}CHR_1$	3560—3600	3580—3610		$O{:}CHR_1$				
$NHX\cdot N{:}CR_1R_2$	3620—3650	3650—3680		$O{:}CR_1R_2$				
$NHX\cdot N{:}CH\cdot CH{:}CH_2$	3660	3670	250—350	$O{:}CH\cdot CH{:}CH_2$	2080 [1]	100—150	1590	~150
$NHX\cdot N{:}CH\cdot CH{:}CHR_1$	3730	3730		$O{:}CH\cdot CH{:}CHR_1$	2170 [1]		1600	
$NHX\cdot N{:}CR_1\cdot CH{:}CHR_2$	3760	3800		$O{:}CR_1\cdot CH{:}CHR_2$	2240 [1]		1500	
$NHX\cdot N{:}CH\cdot CR_1{:}CHR_2$	3770—3830	3820—3850		$O{:}CH\cdot CR_1{:}CHR_2$	2280 [1]		1520	
$NHX\cdot N{:}CH\cdot CH{:}CR_1R_2$				$O{:}CH\cdot CH{:}CR_1R_2$	2350 [1]		1450	
$NHX\cdot N{:}CR_1\cdot CH{:}CR_2R_3$	3770—3790	3870—3950		$O{:}CR_1\cdot CH{:}CR_2R_3$	2390 [1]		1390	
$NHX\cdot N{:}CH\cdot CR_1{:}CR_2R_3$	3870	3890		$O{:}CH\cdot CR_1{:}CR_2R_3$	2450 [1]		1420	
$NHX\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CHR_1$	3790—3950	3880—4070	300—400	$O{:}CH\cdot CH{:}CH\cdot CH{:}CHR_1$	2650 [1, 2]	250	1210	~100
$NHX\cdot N{:}CR_1\cdot CH{:}CH\cdot CH{:}CHR_2$								
$NHX\cdot N{:}C{<}\substack{CH{:}CHR_1\\CH{:}CHR_2}$				$O{:}C{<}\substack{CH{:}CHR_1\\CH{:}CHR_2}$				
$NHX\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CHR_1$	3950—4100	4000—4150	400—500	$O{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CHR_1$	3140 [3]	350	1110	~100
$NHX\cdot N{:}CR_1\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CHR_2$								

[1] Evans and Gillam, J., 1941, 815; 1943, 565. [2] Scheibe, *Ber.*, 1925, **58**, 587. [3] Smakula, *Angew. Chem.*, 1935, **48**, 152.

* Difference between $\lambda_{max.}$ (EtOH) for 2 : 4-dinitrophenylhydrazone and corresponding carbonyl compound.

It is evident that $\lambda_{max.}$ varies not only with the number (n) of ethylenic bonds in the system $NHX\cdot N{:}C\cdot[C{:}C]_n$–, where X stands for the 2 : 4-dinitrophenyl group, but also with the degree of alkyl substitution in the $NHX\cdot N{:}C$– and $NHX\cdot N{:}C\cdot C{:}C$– systems. The bathochromic effects of a conjugated ethylenic bond and an alkyl substituent are of the order of $+\ \Delta\lambda = 100$—150A. and 50—100A., respectively. The former value is considerably smaller than that of $+\ \Delta\lambda =$ *ca.* 250A. found for the bathochromic effect in the 3000—4000 A. region of a conjugated ethylenic bond in conjugated systems such as $Y\cdot[C{:}C]_n\cdot$, where Y is $-C{:}C-$, $-C\vdots C-$, $-C{:}O$, or phenyl. The latter value corresponds to that found for the bathochromic effect of alkyl substituents in the $-C{:}C\cdot C{:}C-$, $-C{:}C-C{:}O$, and $-C{:}C-C\vdots C-$ systems (Hausser, Kuhn, *et al.*, *Z. physikal. Chem.*, 1935, **329**, 363 *et seq.*; Booker, Evans, and Gillam, J., 1940, **1453**; Evans and Gillam, J., 1941, **815**; Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, **1123**; 1942, **64**, 72, 76; Braude and Jones, forthcoming paper). Alkyl substituents have little effect on the intensity, but the $\lambda_{max.}$ of the principal band increases with the number of ethylenic double bonds, as it does in other conjugated systems. A comparison of the light-absorption properties of dinitrophenylhydrazones and the corresponding unsaturated carbonyl compounds is included in Table II.

The subsidiary bands, being more in the nature of inflexions than distinct maxima, are much less well defined than the principal bands, and show only slight correlation with the nature of the parent carbonyl compounds. Bands at *ca.* 2200 and 2600 A. are shown by 2 : 4-dinitrophenylhydrazine itself (Table III) and all the dinitrophenylhydrazones; in addition a band at *ca.* 2800 A. is exhibited by most dinitrophenylhydrazones, and further bands appear at *ca.* 2900 and 3100 A. when $n = 2$.

The effect of change of solvent on the location of the principal maximum [$\Delta\lambda = \lambda_{max.}(CHCl_3)-\lambda_{max.}(EtOH)$] increases from $+\ \Delta\lambda =$ *ca.* 10 to *ca.* 100 A. with n in the system $NHX\cdot N{:}C\cdot[C{:}C]_n\cdot$, whereas ε shows only slight, apparently random variations. Dinitrophenylhydrazine itself, on the other hand, shows a solvent effect opposite in sign ($\Delta\lambda = -\ 70$ A.) (Table III).

TABLE III.

Light absorption of 2 : 4-dinitrophenylhydrazine.

Solvent: EtOH.		Solvent: $CHCl_3$.	
$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.
2190	120	—	—
2580	95	2605	100
3500	145	3435	145
4150	60	4000	50

Light absorption of 2 : 4-dinitroaniline.

Solvent: EtOH.		Solvent: $CHCl_3$.	
$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.
2230	115	—	—
2560	100	2590	110
3350	145	3330	145
~3850	70	~3800	65

DISCUSSION.

The 2 : 4-dinitrophenylhydrazones were examined in preference to simpler derivatives such as the phenylhydrazones or the *p*-nitrophenylhydrazones because of the practical considerations referred to above, although in comparison with the latter derivatives the theoretical treatment of the light absorption of the more complicated systems presents greater difficulties.

In Part I (preceding paper) the term " partial " chromophore was used in order to facilitate the discussion of complex light-absorbing systems. Without attempting an analysis of the light absorption due to the partial chromophore represented by 2 : 4-dinitroaniline (NH_2X), the data given in Table III show that replacement of a hydrogen atom by a second amino-group to give 2 : 4-dinitrophenylhydrazine ($NHX\cdot NH_2$) results in a bathochromic displacement of the long wave-length band by *ca.* 150 A., while the 2600 A. band remains almost unaffected (cf. Macbeth and Price, J., **1935**, 1563). Bathochromic effects of the same magnitude are observed in phenylhydrazine as compared with aniline, and in aniline as compared with benzene (cf. Biquard, *Bull. Soc. chim.*, 1936, **3**, 909), whereas the bathochromic effect of an amino-group when directly attached to certain *substituted* benzenoid or to ethylenic systems is known to be considerably greater, being of the order of $+\Delta\lambda = 300$—600 A. (cf. Ramart-Lucas and Wohl, *Compt. rend.*, **1933**, **196**, 804; Part I; and unpublished results obtained in these laboratories). Hydrazine in aqueous solution exhibits no absorption of appreciable intensity ($\varepsilon > 1$) in the 2100—6000 A. region, and the variochromic properties of the amino-group in the ultra-violet thus fit in well with the classical concept of an auxochrome. The latter, in contradistinction to a chromophore (*e.g.*, an ethylenic double bond), is a group which does not produce a system exhibiting high-intensity absorption in a given region of the spectrum when conjugated with itself, but does produce such a system when conjugated with a chromophore.

In the 2 : 4-dinitrophenylhydrazones of non-conjugated carbonyl compounds the primary amino-group of the hydrazine is replaced by the $\mathrm{{}^-N{:}C{<}}$ group without appreciable alteration in the light absorption. The conjugating power of the $\mathrm{{}^-N{:}C{<}}$ group when attached to a conjugated system through the $>$NH group is thus of the same order as that of the amino-group and, again, it is considerably smaller than when directly joined to an ethylenic system (Evans and Gillam, J., **1943**, 565; unpublished work). The $>$NH group thus has a smaller transmitting (" chromolatory ") capacity for conjugation than, for instance, an ethylenic bond, and this may well be a general characteristic of auxochromes.

In the derivatives of $\alpha\beta$-unsaturated carbonyl compounds, the chromophoric system is extended (to $\mathrm{NHX{\cdot}N{:}C{\cdot}C{:}C^-}$) and $\lambda_{\text{max.}}$ increases, but because of the smaller chromolatory capacity of the $>$NH group, the bathochromic effect of the ethylenic bond is smaller than that usually observed in conjugated systems of the type $\mathrm{Y{\cdot}[C{:}C]_n{\cdot}}$. Further, when the number (n) of double bonds in $\mathrm{NHX{\cdot}N{:}C{\cdot}[C{:}C]_n{\cdot}}$ is increased, the relation $(\lambda_{\text{max.}})^2 = an$, valid in other polyene systems, is obeyed but the constant a has a smaller value than in the case of the system $\mathrm{O{:}C{\cdot}[C{:}C]_n}$ (Fig. 1*a*). The bathochromic effect of alkyl substituents ($+\Delta\lambda_{\text{alk.}} = 50$ A.) is almost fully exerted, however ($\Delta\lambda$ in Table II decreases but slightly with increasing alkyl substitution), and this is particularly interesting in view of the non-operation of this effect in the closely allied semicarbazones (Evans and Gillam, *loc. cit.*). Thus, light absorption data for dinitrophenylhydrazones are more valuable for obtaining structural evidence than similar data derived from the semicarbazones. The system $\mathrm{{}^-CO{\cdot}NH{\cdot}N{:}C{\cdot}C{:}C^-}$, contained in the latter derivatives of $\alpha\beta$-unsaturated carbonyl compounds, provides a further illustration of the variochromic properties of the $>$NH group. The high-intensity absorption ($\lambda_{\text{max.}}$ *ca* 2650 A.) cannot be ascribed to enolisation to $\mathrm{{}^-C(OH){:}N{\cdot}N{:}C{\cdot}C{:}C^-}$, since the same absorption is shown by the corresponding *N*-methylsemicarbazones in which such enolisation cannot occur (Evans and Gillam, *loc. cit.*). It seems clear that the displacement of the maximal absorption, as compared with the $\mathrm{{}^-N{:}C{\cdot}C{:}C^-}$ system present in the $\alpha\beta$-unsaturated oximes, which have $\lambda_{\text{max.}}$ *ca.* 2300 A., is due to the bathochromic effect of the $>$NH group and the partially transmitted conjugation with the carbonyl group.

The phenyl groups in 2 : 4-dinitrophenylhydrazones of the type $\mathrm{NHX{\cdot}N{:}CPh{\cdot}}$ produce a bathochromic effect of the same magnitude ($+\Delta\lambda_{\text{Ph}}$ *ca.* 200 A.) as that of an ethylenic bond, in contrast to other conjugated systems such as the diphenylpolyenes, where $\Delta\lambda_{\text{Ph}} \sim 1{\cdot}5\Delta\lambda_{\text{C=C}}$ (Hausser, Kuhn, *et al.*, *loc. cit.*). Similarly, the bathochromic effect of an acetylenic bond conjugated with the $\mathrm{NHX{\cdot}N{:}C^-}$ system is smaller than that of an ethylenic bond, whereas in other conjugated systems $\Delta\lambda_{\text{C}\equiv\text{C}} \sim \Delta\lambda_{\text{C=C}}$ (Heilbron, Jones, and Raphael, J., **1944**, 186 and unpublished work). Again, α-carboxyl groups produce practically no bathochromic shift, whereas in systems of the type $\mathrm{{}^-(C{:}C)_n{\cdot}CO_2H}$, $+\Delta\lambda_{\text{CO}_2\text{H}} \sim 200$ A.

Bisdinitrophenylhydrazones show normal absorption except in the case of α-diketones, where conjugation occurs between the two hydrazone systems and $\lambda_{\text{max.}}$ increases considerably.

The technique of the light-absorption measurements has been described in Part I (preceding paper).

The authors thank Professor I. M. Heilbron, D.S.O., F.R.S., for his interest in this work and the Rockefeller Foundation for financial assistance. They are also indebted to past and present workers in these Laboratories for providing many of the derivatives examined.

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