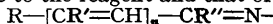


258. *The Absorption Spectra of 2:4-Dinitrophenylsemicarbazones.*

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The absorption spectra of new and previously-prepared 2:4-dinitrophenylsemicarbazones of various aldehydes and ketones are recorded and shown to be, approximately, summation curves of the light absorption due to the reagent and that of the chromophore



where  $n = 0, 1, 2,$  or  $3$  and  $R, R',$  and  $R''$  may be either  $H$  or alkyl. The maxima of the subtraction curves suffer a steady displacement to longer wave-lengths as the conjugated system is lengthened.

In earlier papers (*J.*, 1940, 1453; 1941, 815; 1943, 565; 1945, 432) light-absorption data on carbon compounds containing specific chromophoric groups such as those of unsaturated ketones and their semicarbazones and similar derivatives were collected and classified with the object, among others, of using the data in the determination of molecular structure. In the present communication the absorption spectra of 2:4-dinitrophenylsemicarbazones of various carbonyl compounds are recorded and an attempt is made to correlate the location of the absorption bands with the structure of the compounds and especially the length of the conjugated system present.

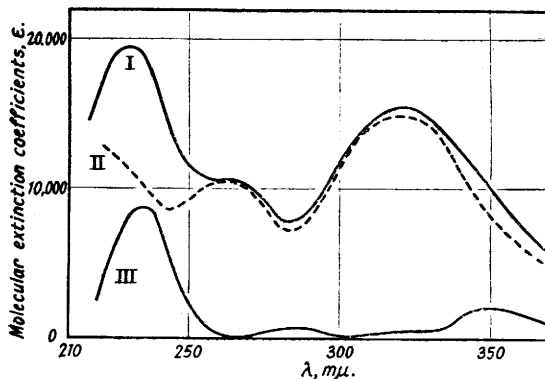
2:4-Dinitrophenylsemicarbazide was first prepared by Knipphorst (*Rec. Trav. chim.*, 1925, 44, 724) who also showed that it formed condensation products with carbonyl compounds. McVeigh and Rose (*J.*, 1945, 713) have more recently shown that it can be used as a means of detection and characterisation of aldehydes and ketones generally, and have recorded the melting points of a number of derivatives of such compounds.

The molecules of these carbonyl derivatives contain two main chromophoric units, namely 2:4-dinitrophenylsemicarbazide itself and the substituted  $>C=N-$  group formed by condensation of the carbonyl group with the active  $-NH_2$  group of the semicarbazide. With  $\alpha\beta$ -unsaturated ketone derivatives the chromophoric groups are those of the substituted semicarbazide itself and the  $CR_n=CH-CR=N-$  group which is, in effect, the  $\begin{array}{c} | & & | \\ -C=C-C=N- \\ | & & | \end{array}$  chromophore normally met with in simple semicarbazones (cf. Evans and Gillam, *J.*, 1943, 565). The work of Ramart-Lucas and her various collaborators (*Bull. Soc. chim.*, 1932, 51, 289) has shown that in a compound having two unconjugated chromophores the light absorption approximates more nearly to a simple summation the more widely separated are the chromophores in the molecule. Thus in the 2:4-dinitrophenylsemicarbazones of unsaturated carbonyl compounds the two compound chromophores are unconjugated but not widely separated so that complete independence is not to be expected.

If we compare the absorption curves of the substituted semicarbazones of simple ketones with those of the corresponding derivatives of  $\alpha\beta$ -unsaturated ketones and of dienones we would further expect to find that the summation curves contain a fixed component (the semicarbazide chromophore) and one which varies in the location of its band with the length of the conjugated system responsible for it. Thus in any observed absorption curve of a 2:4-dinitrophenylsemicarbazone if we subtract the known absorption of the reagent the resulting subtraction curve should be that of the  $R-[CR'=CH]_n-CH=N-$  chromophore (where  $n = 0, 1, 2, 3,$  etc., and  $R$  and  $R'$  may be either  $H$  or alkyl groups).

The numerical data are given in Table I, whilst Figs. 1, 2, and 3 show the absorption curves of only a few of the more typical examples. The occurrence of low-intensity absorption bands between  $270$  and  $360m\mu$  in some of the subtraction curves is still unexplained, but this does not appear to affect the main conclusions.

FIG. 1.



Absorption spectra in alcohol:

- I. cycloHexanone 2:4-dinitrophenylsemicarbazone.
- II. 2:4-Dinitrophenylsemicarbazide.
- III. Subtraction curve.

TABLE I.  
Spectroscopic Data on 2 : 4-Dinitrophenylsemicarbazones.

Parent carbonyl compound.	$\lambda_{\max.}, \text{A.}$	$\epsilon.$	Subtraction curve.		No. of ethylene links or equivalent.
			$\lambda_{\max.}, \text{A.}$	$\epsilon.$	
<i>Simple aldehydes and ketones.</i>					
Acetaldehyde .....	2285	19,400	2325	8,400	}
	2640	12,600			
	3200	16,500			
Methyl ethyl ketone .....	2275	20,000	2300	8,800	
	2630	11,800			
	3200	15,900			
Methyl <i>n</i> -propyl ketone .....	2280	19,200	2300	8,000	
	2650	11,000			
	3205	15,800			
<i>cyclo</i> Hexanone .....	2295	19,300	2325	8,400	
	2640	10,800			
	3205	15,400			
<i><math>\alpha\beta</math>-Unsaturated aldehydes and ketones.</i>					
Mesityl oxide .....	2600	22,600	2600	12,000	}
	3220	17,400			
3-Methylpent-3-en-2-one .....	2600	24,000	2610	13,600	
	3225	15,800			
1-Methylcyclohexen-3-one .....	2635	29,800	2640	19,400	
	3235	19,400			
Crotonaldehyde .....	2625	32,200	2640	21,800	
	3220	19,100			
<i>Dienones.</i>					
$\psi$ -Ionone .....	3075	40,000	3000	27,500	}
Hepta-3 : 5-dien-2-one .....	2875	37,700	2850	30,100	
<i>Aromatic compounds.</i>					
Benzaldehyde .....	2725	23,800	2790	15,600	}
	3145	22,300			
Acetophenone .....	2650	25,000	2650	14,800	
	3175	20,000			
Cinnamaldehyde .....	3220	45,000	3250	30,200	}
Benzylideneacetone .....	3150	39,700	3100	25,300	
Citrylidencrotonaldehyde .....	3290	41,500	3360	28,200	4
2 : 4-Dinitrophenylsemicarbazide ...	2610	10,500	}	—	
	3220	14,900			

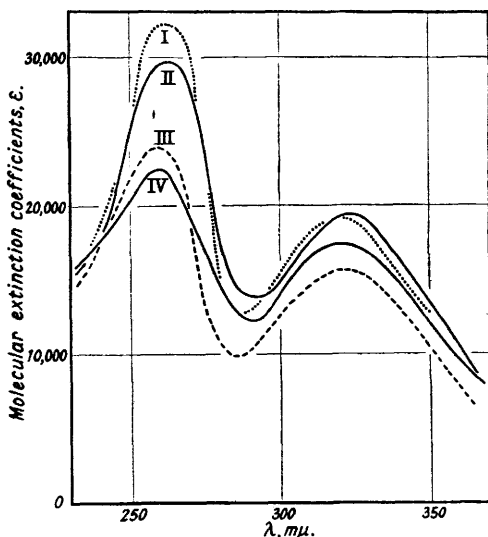
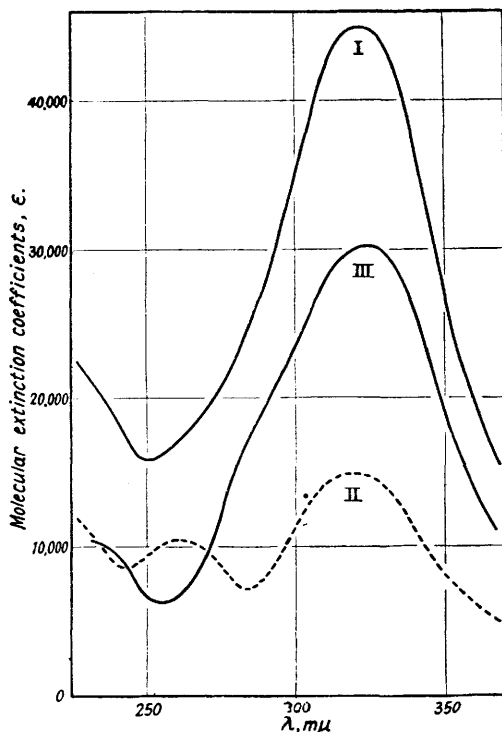


FIG. 2.  
Dinitrophenylsemicarbazones (absorption spectra in alcohol):  
I. Crotonaldehyde.  
II. 1-Methylcyclohexen-3-one.  
III. 3-Methylpent-3-en-2-one.  
IV. Mesityl oxide.

The subtraction-curve data in Table I show the steady displacement of the maxima to longer wave-lengths as the length of the conjugated system in the non-semicarbazide part of the molecule increases. This is shown more clearly in Fig. 4. The fact that the two types of aromatic carbonyl derivative show displacements which are respectively equivalent to  $2\frac{1}{2}$  and  $3\frac{1}{2}$  ethylene linkages supports the suggestion of Kuhn, Häusser, *et al.* (*Z. physikal. Chem.*, 1935, 29, B, 363) that a benzene nucleus in conjugation with one or more ethylene linkages is equivalent to  $1\frac{1}{2}$  of such bonds.

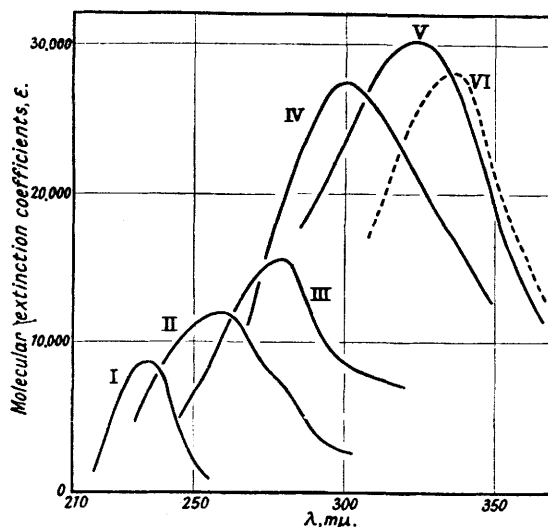
FIG. 3.



Absorption spectra in alcohol :

- I. Cinnamaldehyde 2 : 4-dinitrophenylsemicarbazone.  
 II. Reagent.  
 III. Subtraction curve.

FIG. 4.



2 : 4-Dinitrophenylsemicarbazone subtraction curves :

- I. Simple ketone (cyclohexanone).  
 II.  $\alpha\beta$ -Unsaturated ketone (mesityl oxide).  
 III. Simple aromatic aldehyde (benzaldehyde).  
 IV. Dienone ( $\psi$ -ionone).  
 V. Unsaturated aromatic aldehyde (cinnamaldehyde).  
 VI. Trienal (citrylidene crotonaldehyde).

The validity of the generalisation that two unconjugated chromophores in a molecule produce an approximate summation of the effects due to each can be checked within this particular series, since the observed absorption of the 2 : 4-dinitrophenylsemicarbazones when

TABLE II.

Comparison of Direct Absorption Data on Semicarbazones with Subtraction Curves via the 2 : 4-Dinitrophenylsemicarbazones.

Parent carbonyl compound.	Direct absorption spectrum of semicarbazone.		Subtraction curve via 2 : 4-dinitrophenylsemicarbazone.	
	$\lambda_{\text{max.}}$ , A.	$\epsilon$ .	$\lambda_{\text{max.}}$ , A.	$\epsilon$ .
cycloHexanone .....	2295	11,200	2325	8,400
Mesityl oxide .....	2600	12,000	2600	12,000
Crotonaldehyde .....	2645	24,000	2640	21,800
1-Methylcyclohexen-3-one. ...	2655	25,700	2640	19,400
$\psi$ -Ionone .....	2995	45,400	3000	27,500
Hepta-3 : 5-dien-2-one .....	2900	37,000	2850	30,100
Benzaldehyde .....	2825	19,900	2790	15,600
Acetophenone .....	2715	17,780	2650	14,800

corrected for the separate absorption of the reagent itself should yield a subtraction curve comparable with the known and directly observed absorption spectra of the simple semicarbazones. The available data are given in Table II, and, considering the number of variables concerned in obtaining the data, the general agreement is good, being better in terms of location of the band than where intensities are concerned. The values for  $\psi$ -ionone are noticeably discrepant in this latter respect.

## EXPERIMENTAL.

1-Methylcyclohexen-3-one was prepared by condensation of formaldehyde and acetoacetic ester followed by ring-closure of the methylenedi-acetoacetic ester (Knoevenagel, *Annalen*, 1894, **281**, 94); b. p. 200°.

3-Methylpent-3-en-2-one was prepared by condensation of acetaldehyde and methyl ethyl ketone (Hinkel, *J.*, 1931, 817). The ketone was crystallised from benzene to constant m. p., but the N content was low (Found: N, 19.6. Calc.: N, 21.8%). This might have been due to retention of solvent as the spectroscopic data were quite normal. Attempted purification by chromatography gave slight evidence of lack of homogeneity, but no increase in purity was in fact achieved.

$\psi$ -Ionone was prepared by condensation of acetone and citral (Stiehl, *J. pr. Chem.*, 1898, **58**, 79) and crystallised successively from chloroform and chlorobenzene.

We are indebted to Dr. E. R. H. Jones for a sample of citrylidencrotonaldehyde which was isolated from the products of the condensation of citral with crotonaldehyde (cf. Batty *et al.*, *J.*, 1937, 756; 1939, 1559). The specimen used had  $\lambda_{\max}$ . 3140 Å.;  $\epsilon = 14,500$ .

2:4-Dinitrophenylsemicarbazones.—These were prepared by dissolving 2:4-dinitrophenylsemicarbazide (0.5 g.) in alcohol (80 ml.) and adding to the boiling solution slightly less than the theoretical amount of the carbonyl compound dissolved in the minimum of alcohol. After addition of concentrated hydrochloric acid (2 drops) the solution was boiled for ten minutes after which the precipitated derivative was filtered off, being usually only very sparingly soluble in alcohol even at the boiling point. For recrystallisation chloroform was found to be the most useful solvent and derivatives were recrystallised to constant melting point, two or three crystallisations being usually sufficient. All the 2:4-dinitrophenylsemicarbazones in Table III are new except that of methyl ethyl ketone (cf. McVeigh and Rose, *loc. cit.*).

TABLE III.

## 2:4-Dinitrophenylsemicarbazones.

Aldehyde or ketone.	M. p. of deriv.	Formula.	Nitrogen, %.		Recrystallised from:
			Calc. or required.	Found.	
Methyl ethyl ketone .....	235° (decomp.)	C <sub>11</sub> H <sub>13</sub> O <sub>5</sub> N <sub>5</sub>	23.7	23.7	Chloroform
Mesityl oxide .....	207 "	C <sub>13</sub> H <sub>15</sub> O <sub>5</sub> N <sub>5</sub>	21.8	21.4	Chloroform
3-Methylpent-3-en-2-one ...	236.5 "	C <sub>13</sub> H <sub>15</sub> O <sub>5</sub> N <sub>5</sub>	21.8	19.6	Benzene
1-Methylcyclohexen-3-one	227.5 "	C <sub>14</sub> H <sub>15</sub> O <sub>5</sub> N <sub>5</sub>	21.0	20.7	Chloroform
$\psi$ -Ionone .....	227 "	C <sub>20</sub> H <sub>25</sub> O <sub>5</sub> N <sub>5</sub>	16.9	16.1	Chlorobenzene
Hepta-3:5-dien-2-one .....	240 "	C <sub>14</sub> H <sub>15</sub> O <sub>5</sub> N <sub>5</sub>	21.0	20.4	Alcohol
Citrylidencrotonaldehyde	207 (no decomp.)	C <sub>21</sub> H <sub>25</sub> O <sub>5</sub> N <sub>5</sub>	16.4	16.1	Alcohol

Absorption spectra were determined by standard methods using a Hilger E3 quartz spectrograph and a Spekker photometer. Purified alcohol was used as solvent throughout, although the very low solubility of the 2:4-dinitrophenylsemicarbazones made this difficult at times. The high intensity of absorption in some cases made it possible to use very dilute solutions for the determination, and the concentrations usually ranged between 0.03 and 0.003% only. The solutions were made by dissolving 2—3 mg. of the compound in hot alcohol, cooling, and making up to suitable volume, *e.g.*, 100 ml. All determinations were made in duplicate, the  $\lambda_{\max}$ . and  $\epsilon_{\max}$ . values being taken from the mean curves.

Our thanks are due to Miss McVeigh and Dr. F. L. Rose for specimens of a number of the compounds examined.

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