

# A STUDY OF THE REFRACTIVITY OF UNSATURATED COMPOUNDS.

## PART I.

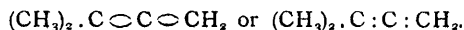
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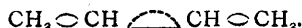
Much work has been done on this subject, but the theory is still incomplete, and needs revision in parts. The object of this paper is to clear the ground for an advance in the direction of a better understanding of the anomalies of complicated unsaturated compounds, and especially to analyse these complex anomalies so as to obtain accurate estimations of their different elements. Auwers, in particular, has done much valuable and comprehensive work on the subject of the refractivities of unsaturated compounds, but nevertheless there is room for independent work along these lines.

### THE ETHENOID GROUP.

It is suggested that the symbol  $|\bigcirc|$  be used as an alternative to the ordinary one  $||$ , and in place of the inaccurate  $||=|$ . The former is theoretically the more accurate. Thus valerylene would be



The symbol  $|\bigcap|$  is proposed for conjugated linkings, first, because it implies the existence of a field of force between the conjugated systems, and secondly, because it points to an optical effect due to the passage of luminous vibrations through this field of a definite magnitude. Thus—



In certain cases the use of the symbol  $||=|$  is retained for reasons of convenience, but it would be useful to limit its use as much as possible.

Ethenoid links may be *unsubstituted* and *substituted*, and the work of Eykman in the direction of classifying the different types of unsaturation involving ethenoid groups is of fundamental importance.

It is not generally recognized that ethylene ( $\text{C}_2\text{H}_4$ ) and benzene ( $\text{C}_6\text{H}_6$ ) are both cases of unsubstituted systems involving ethenoid linkings, and are therefore comparable. This is shown by the fact that the optical effect for one  $||$  is the same in the two. Moreover, they stand at the head of their respective series—

$\text{CH}_2 : \text{CH}_2.$			$\text{C}_6\text{H}_6.$		
	$\text{M}_a$	10'74		$\Sigma$	25'93
less	2 $\text{CH}_2$	9'20		$\Sigma n r_a$	21'24
	$  = $	+ 1'54		3 $  = $	4'69
				$  = $	1'56

Benzene shows no anomaly due to conjugation. This fact, together with the similarity of the values  $|\vdots|$  in the two cases, must be taken into account when the chemical condition of benzene is considered. In drawing up the scheme of representation, it has been found necessary to revise Thiele's system of representation and Brühl's explanation of the absence of anomaly due to conjugation. If the symbol  $|\text{---}|$  (used in the sense already indicated) be admitted, then Thiele's formula for benzene does not represent the facts, or, at any rate, the above symbol is used in a different sense from that employed by him. From the present point of view, it will be better to omit the curved dotted lines in the benzene formula, and use them only when there may be supposed to be a field of force due to residual affinity. This would augment the refractivity of the compound and thus produce a positive anomaly. The calculation of a negative anomaly for benzene and its homologues has been avoided, so that the standards of comparison for the aliphatic and aromatic classes of compounds are the same. Thus—

Hexane•	→	Cyclohexane	→	Benzene
$M_a$ 29'80 (—H <sub>2</sub> )		27'68 (—6H)		21'20
$M_a$		3   :		4'68 (3 × 1'56)
				25'88
				25'93
Ethylene	→			Benzene
$M_a$ 3(C <sub>2</sub> H <sub>4</sub> ) 32'22	(—6H)			25'74

Turning to the question of unsaturation in aliphatic compounds, it is found that the augmentation for each substitution of the group  $\cdot\text{CH} : \text{CH} \cdot$  is 0'11 instead of 0'15 as given by Eykman. Thus—

$$|\vdots|^{(0)} 1'54; |\vdots|^{(1)} 1'65; |\vdots|^{(2)} 1'76; |\vdots|^{(3)} 1'87; |\vdots|^{(4)} 1'98.$$

This augmentation, which is recognized to be due to the mutual action of the ethenoid linking and the methyl group, may be symbolically shown by the scheme—



In reality it is due to the mutual action of the methyl group and the contiguous unsaturated carbon atom, the penultimate carbon atom having no effect. Reasons for this conclusion will be given later.

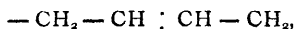
The same principle may be applied to aromatic compounds. Thus the formula for toluene would be



In this series the augmentation is +0'26, which may be due to the fact that the group  $\text{C}_6\text{H}_5$  is more unsaturated than the group R.

If the substituents be  $\text{C}_2\text{H}_5$  — or  $\text{C}_3\text{H}_7$ , the augmentation is still 0'26, that is, the additional methylene groups do not produce any effect.

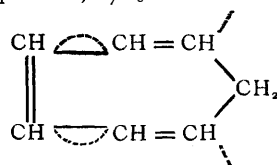
Again, the approximation of two methylene groups, as in *o* xylene, causes a diminution of the augmentation by +0'26. These are general rules. At any rate, the principle may be applied to all cases where the grouping  $\cdot\text{C}(\text{CH}_3) : \text{C}(\text{CH}_3) \cdot$  occurs. This is not the case in the grouping



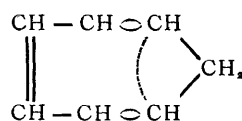
probably because the methylene groups are not proximate constituents of the molecules in which they occur. Interaction is thus suggested in the former case.

*The Refractivities of the Benzene Homologues.*

Substances.	$M_a$ .	$\Sigma nr_a$ .	$\Delta$ .
Benzene, $C_6H_6$ ... ..	25'93	—	—
Toluene, $C_6H_5 \cdot CH_3$ ...	30'79	30'79	$\pm 0$
<i>p</i> Xylene, $C_6H_4(CH_3)_2$ ...	35'70	35'65	+ 0'05
<i>m</i> " " " ...	35'65		
<i>o</i> " " " ...	35'46	35'40	+ 0'06
Ethyl benzene, $C_6H_5 \cdot C_2H_5$	35'33	35'39	— 0'06
Mesitylene, $C_6H_3(CH_3)_3$ ...	40'33	40'35	— 0'02
1 : 2 : 6 Trimethyl benzene	40'35 (B.)		
	40'23 (L. & J.)	40'26	— 0'03
<i>p</i> Methyl ethyl, $C_6H_4(CH_3)C_2H_5$			
<i>m</i> Propyl benzene, $C_6H_5 \cdot C_3H_7$	40'00	40'00	$\pm 0$
<i>o</i> " " " "	40'10	—	—
Tropilidene, $C_7H_8$			



Thiele.



Proposed formula.

	$M_a$ 31'57
$C_7H_8$	25'84
3   :   <sup>(1)</sup>	4'68 (3 × 1'56)
conj.	1'06
$\Sigma nr_a$	31'58

The only anomaly is one equal to the refractivity of an atom of hydrogen, 1'06, and, as already shown, can be indicated by a curved dotted line. An inspection of the formula shows that the two reacting ethenoid links are separated by a methylene group. It follows that it is necessary to suppose that the partial valencies or residual affinities can act across the gap. There is at present no explanation why the benzene and tropilidene ethenoid links should show no augmentation for conjugation. It is to be observed that the augmentation for  $-CH : CH \text{---} CH_2-$  has also disappeared. It thus seems that the absence of these augmentations is connected with the ring structure of the compounds. The exact reason for this is not at present apparent.

## THE ACETYLENE LINKAGE.

This type of unsaturation does not seem to have been so successfully dealt with as the analogous ethenoid linkage. Nevertheless, careful consideration shows that, as in the latter case, at least three types occur which are dependent upon the number of substitutions which have taken place—

Unsubstituted.	Singly substituted.	Doubly substituted.
$CH : CH$	$-CH_2 \cdot C : CH$	$-CH_2 - C : C - CH_2 -$
$\Delta$ + 1'98	+ 2'16	+ 2'36
	+ 0'18	+ 0'20

*Unsubstituted.*—Acetylene is the only example of this type of linkage.

CH : CH					
$M_a$	9.06	$M_D$	9.11		
$\Sigma nr_a$	7.08		7.12		
$\Delta$	+ 1.98	$\Delta$	+ 1.99		

*Singly substituted.*—

Propargyl ethyl ether (Brühl)—	$M_a$	$\Sigma nr_a$	$\Delta$
CH : C.CH <sub>2</sub> —O—C <sub>2</sub> H <sub>5</sub>	24.54	22.48	+ 2.06

Propargyl acetate—

CH : C.CH <sub>2</sub> .C(OCH <sub>3</sub> ) : O	24.57	22.50	+ 2.05
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*n* Amyl acetylene—

CH : C.(CH <sub>2</sub> ) <sub>4</sub> .CH <sub>3</sub> (Moureaux)...	32.29	30.08	+ 2.21
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*n* Hexyl acetylene—

CH : C.(CH <sub>2</sub> ) <sub>5</sub> .CH <sub>3</sub> ( „ )	36.84	34.68	+ 2.21
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Ethyl  $\Delta\gamma$  butinene carboxylate—

CH : C.CH <sub>2</sub> .CH <sub>2</sub> .CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	33.82	31.70	+ 2.12
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Average  $\Delta$  + 2.12

*Doubly substituted.*—

Heptidene C <sub>7</sub> H <sub>12</sub> (unspecified, Br.)	32.46	30.08	+ 2.38
probably CH <sub>3</sub> .C : C.C <sub>4</sub> H <sub>9</sub> .			

Amyl propiolic acetal—

CH <sub>3</sub> .(CH <sub>2</sub> ) <sub>4</sub> .C : C.CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	58.89	56.54	2.35
		$\Delta$	+ 2.36


If Brühl's unspecified hydrocarbon heptidene be compared with amyl acetylene, it is found that they are isomeric, but according to the principles first pointed out by Eykman for the olefines there should be a small difference between the singly unsubstituted and doubly unsubstituted types.

CH : C.(CH <sub>2</sub> ) <sub>4</sub> .CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub> .C : C.CH <sub>3</sub>
Amyl acetylene	Heptidene
$M_a$ 32.29	32.46
$\Delta$ + 0.17	

Cases of conjugation of the acetylene linkage and other groups are known, some of which may now be considered.

Ethyl propiolate—	$M_a$	$\Sigma nr_a$	$\Delta$
CH : C  C : O			
OC <sub>2</sub> H <sub>5</sub>	25.12	24.62	+ 0.50

Methyl amyl propiolate—

CH <sub>3</sub> .(CH <sub>2</sub> ) <sub>4</sub> .C : C  C : O			
OCH <sub>3</sub>	44.14	43.26	+ 0.88

Amyl propiolic acid—

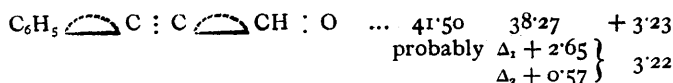
CH <sub>3</sub> .(CH <sub>2</sub> ) <sub>4</sub> .C : C—C : O			
OH	39.86	38.66	+ 1.20

There is a progressive increase of + 0.35 from the first to the third.

## Phenyl acetylene—



## Phenyl propiolic aldehyde—



## Diphenyl diacetylene—



## Distribution uncertain.

The ethenoid group may be conjugated

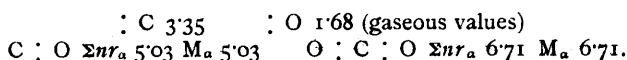
- (a) With another ethenoid group.
- (b) With a carbonyl group.
- (c) Two carbonyl groups may be conjugated.

## THE CARBONYL GROUP.

A study of the groups  $\text{—C:O...}$ ,  $\text{—C:N}$  shows that the oxygen and nitrogen atoms possess exactly the same values as the singly linked oxygen and nitrogen due to the carbon atoms alone.

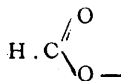
This is shown by a study of the refractivities of gaseous carbon monoxide and dioxide.\*

The values are—



The group  $\text{>C:O}$  appears in the aldehydes, ketones, and acids. As a rule,  $\Sigma n r_a = \text{Ma}$ , but in certain cases there are augmentations which evidently depend upon the nature of the substituents.

Thus the group



carries an augmentation.

## Alkyl chlorides—

	$\text{Ma}$ .	$\Sigma n r_a$ .	$\Delta$ .
$\text{O} = \text{C} \begin{array}{l} \text{Cl} \\ \diagup \diagdown \end{array}$	17·32	16·84	+ 0·48
$\text{O} = \text{C} \begin{array}{l} \text{Cl} \\ \diagup \diagdown \\ \text{CH}_3 \end{array}$	16·74	16·45	+ 0·29
$\text{O} = \text{C} \begin{array}{l} \text{Cl} \\ \diagup \diagdown \\ \text{C}_3\text{H}_7 \end{array}$	25·66	25·65	—

The anomaly evidently depends upon the number of chlorine atoms attached to the unsaturated carbon and to the complexity of the alkyl group. When the hydrocarbon radicle contains at least three carbon atoms the anomaly disappears.

\* See *Chemical News*, 1917, cxv., p. 277.

There are several cases which are interesting, but which cannot be dealt with so simply.

*Conjugation of an Ethenoid and Carbonyl Group.*

$-\text{CH} : \text{CH} \text{---} \text{C} : \text{O}$	
Acrolein, $\text{C}_3\text{H}_4\text{O}$	$M_a$ 16.01
$\Sigma nr_a (\text{C}_3\text{H}_6\text{O} - \text{H}_2)$	13.81
$\begin{array}{c}   :   \\   :   \end{array}$	1.65
Conj.	0.55
	$\Sigma nr_a$ 16.01
	$M_a$ 16.01

Methyl oxide—	$M_a$ .	$\Sigma nr_a$ .	$\Delta$ .
$(\text{CH}_3)_2\text{C} : \text{CH} \text{---} \text{C}(\text{CH}_3) : \text{O} \dots \dots \dots$	30.13	25.59	+0.54
Ethyl crotonate—			
$(\text{CH}_3)_2\text{C} : \text{CH} \text{---} \text{C}(\text{OC}_2\text{H}_5) : \text{O} \dots \dots \dots$	31.49	30.98	+0.51
Angelic acid—			
$\text{CH}_3 : \text{CH} : \text{C}(\text{CH}_3) \text{---} \text{C}(\text{OH}) : \text{O} \dots \dots \dots$	26.95	26.38	+0.57
Hexenic acid—			
$\text{CH}_3 : (\text{CH}_2)_2 : \text{CH} : \text{CH} : \text{C}(\text{OH}) : \text{O} \dots \dots \dots$	31.56	30.99	+0.57
Ethyl fumarate—			
$\text{O} : \text{C}(\text{OC}_2\text{H}_5) \text{---} \text{CH} : \text{CH} \text{---} \text{C}(\text{OC}_2\text{H}_5) : \text{O} \dots \dots \dots$	42.90	41.76	+0.57 × 2

It is concluded that the anomaly for conjugation of an ethenoid and carbonyl group is +0.57 approx., or half the conjugation due to two ethenoid groups.

*The Conjugation of Two Carbonyl Groups.*

Brühl and others have shown that when two carbonyl groups are in conjugation there is no anomaly. This is in some cases not quite apparent if the values  $\Sigma nr_a$  are calculated from the average atomic numbers.

	$M_a$ .	$\Sigma nr_a$ .
Glyoxal, $\text{O} : \text{CH} - \text{CH} : \text{O}$	11.86	11.60
or $2r_a (\text{H} \cdot \text{CO}_2\text{H} - \text{OH}) = 2 (8.52 - 2.56)$		11.92

The reason is that there are small anomalies for the groups  $\text{O} : \text{CH} \cdot$  which are carried into the more complicated compound.

The carbonyl group may be conjugated with

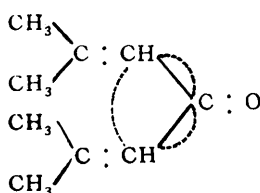
- (a) an ethenoid group,
- (b) another carbonyl group.

(a) Acetyl ketone,  $\text{C}_4\text{H}_4\text{O}_2$ .  $M_a$  20.07

$\text{O} : \text{C}(\text{CH}_3) \text{---} \text{CH} : \text{C} : \text{O}$	
$\text{C}_4\text{H}_4$	14.16
2O	4.48
$\frac{1}{2}   :  $	+0.88
$\Delta$	+0.55
$\Sigma nr_a$	20.07
$M_a$	20.07

The group  $\cdot\text{CH} : \text{C} : \text{O}$  is a condensed ethenoid and carbonyl group. The value of the unsaturated linkage is only half that of an ethenoid linkage, and the effect due to conjugation is similar to that due to the conjugation of an ethenoid and carbonyl group. This seems to show that the augmentation due to conjugation is due to the influence of the two singly linked unsaturated carbon atoms, and not to the unsaturated groups as a whole.

(b) Phorone,  $\text{C}_9\text{H}_{14}\text{O}$ .  $M_a$  45'39



It is found that

$$\begin{array}{r} N_a \quad 45'39 \\ \Sigma nr_a \quad 43'08 \\ \hline \Delta \quad 2'31 \\ \Delta_i \quad 2 \times \text{anom. } 1'14 \quad (2 \times 0'57) \\ \Delta_s \quad 1'17 \quad (\text{for action across gap}). \end{array}$$

The second anomaly cannot be accounted for by means of the ordinary theory. It is concluded that the ethenoid linkages interact across the gap. The anomaly for this is  $\Delta_s = +1'17$ .

The following results have been obtained :—

No. of Ethenoid Groups.	Groups in Conjugation.	Augmentation.
2	Two ethenoid groups ...	+ 1'08 (2 × 0'54)
1	One ethenoid and one carbonyl group ...	+ 0'54 (1 × 0'54)
0	Two carbonyl groups ...	0

The reason for the above rule is that the anomaly is caused by the interaction of two contiguous singly linked unsaturated carbon atoms  $\cdot\text{C} \text{---} \text{C} \cdot$ . If one or two of them be in union with the atom  $\cdot\text{O}$ , a part or the whole of the anomaly is suppressed. The significance of the curved dotted line is thus at once apparent.

#### THE NITRITES, NITRATES, AND NITRO COMPOUNDS.

This very interesting series has given rise to considerable speculation as to the nature of the  $\text{NO}_2$  group in nitric acid and the nitrates. In dealing with these compounds we follow along the lines already indicated.

$$\begin{array}{ll} r_a(\text{N}) \quad 2'30 \text{ O'' for nitro compounds} & 2'16 \\ 2'50 \text{ >O for nitrites and nitrates} & 1'80 \end{array}$$

#### Nitro Compounds.

	$M_a$	$\Sigma nr_a$	$\Delta$
$\text{C}_3\text{H}_7 - \text{NO}_2$ ... ..	21'30	21'40	— 0'10
$\text{C}_6\text{H}_{11} - \text{NO}_2$ ... ..	30'57	30'60	— 0'03
$\text{C}_8\text{H}_{17} - \text{NO}_2$ ... ..	44'58	44'40	+ 0'18

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## Nitriles.

$C_3H_7-O \text{ --- } N : O \text{ ...}$	22'10	21'08	+ 1'02
$C_5H_{11}-O \text{ --- } N : O \text{ ...}$	31'44	30'28	+ 1'16

## Nitrates.

$H.O.O \text{ --- } N : O \text{ ...}$	10'00 (D)	9'90 (a)	
or $H.O \text{ --- } N \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$			
$C_5H_{11}.O.O \text{ --- } N : O \text{ ...}$	33'18	32'08	+ 1'10
or $C_5H_{11}. \text{ --- } N \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$			

It follows that the anomalies are equal to the refractivity of hydrogen, and that the constitutions of the compound are as indicated. In the case of the nitrates there is thus no evidence for the peroxide structure.

## OXIMINO GROUP.

$-CH : N -$ $\Delta + 0'78^*$	$-CH : NH$ $>C : NH$	$>C : N \text{ --- } OH$ + 1'35		
		$M_a.$	$\Sigma m_a.$	$  :  .$
$HO.N : C(CH_3)_2 \text{ ...}$	...	20'21	18'87	+ 1'34
$\{ HO.N : CH \text{ --- } C(CH_3) : O \text{ ...}$	...	21'39	20'36	1'03
$\{ HO.N : C(CH_3) \text{ --- } C(CH_3) : O$		25'93	24'96	0'97
			mean	1'00
$\{ HO.N : C(CH_3) \text{ --- } C(OC_2H_5) : O$		31'50	31'07	+ 0'43
$\{ HO.N : CH \text{ --- } C(CH_3) : O$		21'39	20'37	+ 1'02
				+ 1'05
$HO.N : C \begin{smallmatrix} \diagup C(CH_3) : O \\ \diagdown C(OC_2H_5) : O \end{smallmatrix}$		37'37	35'81	+ 1'56
		$\{ \Delta_1$	+ 0'43	
		$\Delta_2$	+ 1'02	+ 1'45
$HO.N : C(CH_3) \text{ --- } C(OC_2H_5) : O$		31'50	31'06	+ 0'44
$HO.N : C(CH_3) \text{ --- } C(OH) : O$		22'45	21'83	+ 0'62
$N : C \text{ --- } C \text{ --- } C : O$ $\quad \quad \quad \parallel \quad \quad  $ $\quad \quad \quad HO-N \quad \quad OC_2H_5$		32'83	30'82	+ 2'01
		$\{ \Delta_1$	+ 0'43	
		$\Delta_2$	+ 1'57	+ 2'00
$N : C \text{ --- } C \text{ --- } C : O$ $\quad \quad \quad \parallel \quad \quad  $ $\quad \quad \quad HO-N \quad \quad OH$		23'78	21'59	+ 2'19
		$\{ \Delta_1$	+ 0'62	
		$\Delta_2$	+ 1'57	+ 2'19

No comment need be made on these results. Owing to considerations of space, these are reserved. They are certainly very significant, and show that the experimental results obtained by Müller and Bauer can be explained by hypotheses similar to those already adopted.

\* The value +0'78 is about equal to half the augmentation due to an ethenoid link, because the atom  $: N -$  does not contribute to it. The same thing is seen in pyridene. In this respect  $: N -$  resembles  $: O$ .