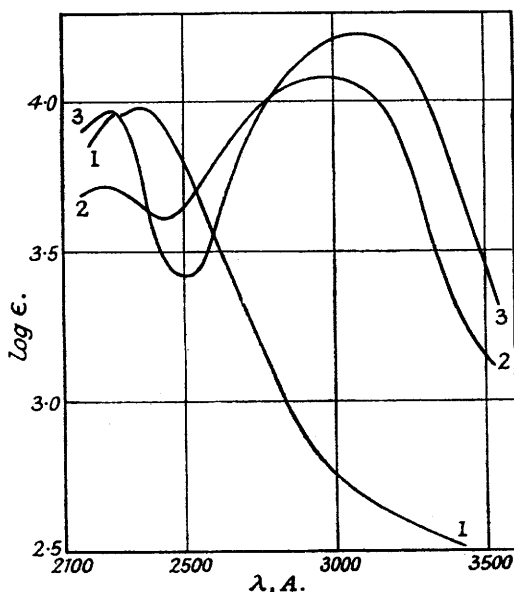


207. *Studies in Light Absorption. Part IV. Nitro-olefins.*

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The ultra-violet light absorption of a number of compounds containing the conjugated chromophoric systems  $C:C\cdot X$ ,  $C:C:C\cdot X$ , and  $Ph\cdot C:C\cdot X$  where  $X = NO_2$  has been examined, and found to be similar to that of the corresponding systems where  $X = C:C$ ,  $C:N$ ,  $C:O$ , etc.

It is well known that chromophoric systems of the type  $C:C\cdot X$ , where  $X$  is a covalently unsaturated group such as  $C:C$ ,  $C:N$ , or  $C:O$ , all exhibit selective high-intensity absorption in the 2200 Å. region (cf. Braude, *Ann. Reports*, 1945, **42**, 105). The spectral properties of nitro-olefins ( $X = NO_2$ ) have not hitherto been recorded. Since the conjugating properties of the nitro-group when attached to a phenyl group are known to resemble those of other covalently unsaturated groups (*e.g.*, nitrobenzene, styrene, benzaldehyde, and its *N*-methylimide all



Light absorption (in ethanol) of :

1.  $CHMe:CH\cdot NO_2$ .
2.  $CHMe:CH\cdot CH:CH\cdot NO_2$ .
3.  $Ph\cdot CH:CH\cdot NO_2$ .

exhibit similar ultra-violet light absorption due to the chromophoric system  $Ph\cdot X$ ), the nitro-olefin system  $C:C\cdot N\begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$  would also be expected to absorb intensely in the 2200 Å. region. Data for a number of representative compounds (Table; Fig.) show that this expectation is fulfilled, but the maxima are situated at somewhat longer wave-lengths than in the formally related  $C:C\cdot C:O$  and  $C:C\cdot C\begin{smallmatrix} \diagup O \\ \diagdown OH \end{smallmatrix}$  systems.

Although an isolated nitro-group, just as a carbonyl group, gives rise to a low-intensity band near 2700 Å. (Zelinsky and Rosanoff, *Z. physikal. Chem.*, 1912, **78**, 629; Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 504; Kortüm, *Z. physikal. Chem.*, 1939, *B*, **43**, 271), nitro-olefins exhibit no band corresponding to the displaced carbonyl band at 3200 Å. shown by  $\alpha\beta$ -ethylenic carbonyl compounds. The solvent effects in the two systems are similar,  $\lambda_{max}$  (ethanol) being higher than  $\lambda_{max}$  (*n*-hexane) by an average of *ca.* 100 Å. with the nitro-olefins,

and by *ca.* 70 Å. with  $\alpha\beta$ -ethylenic carbonyl compounds (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72; Evans and Gillam, *J.*, 1945, 432). On the other hand, in the case of the nitro-olefins, vibrational structure appears to be more pronounced in ethanol than in hexane, which is unexpected since the former is generally the more highly solvating solvent.

Lengthening of the conjugated chain as in the  $\alpha$ -nitrobutadiene and  $\beta$ -nitrostyrene systems, *i.e.*, C:C:C:NO<sub>2</sub> and Ph·C:C·NO<sub>2</sub>, respectively, results in the expected increase in  $\lambda_{\max}$ , and the positions of the long wave-length bands are again 200–300 Å. higher than those of the corresponding bands shown by the C:C·C:C:O and Ph·C:C·C:O systems. The persistence of shorter wave-length bands, probably to be ascribed to the partial chromophore C:C·NO<sub>2</sub>, is peculiar to the nitro-compounds.

The effects of auxochromic substituents are similar to those observed in other systems (cf. Part III, *J.*, 1946, 948);  $\lambda_{\max}$  is increased by alkyl and halogen substituents attached to the  $\alpha\beta$ -ethylenic bond, thus,  $\Delta\lambda_{\text{Me}} = \text{ca. } 100 \text{ Å.}$ , and  $\Delta\lambda_{\text{Br}} = \text{ca. } 300 \text{ Å.}$  in the nitro-ethylenes. In the nitrostyrene system the effects are smaller or negative, thus, for  $\beta$ -substituents  $\Delta\lambda_{\text{Me}} = -50 \text{ Å.}$ ,  $\Delta\lambda_{\text{Cl}} = 100 \text{ Å.}$ , and  $\Delta\lambda_{\text{Br}} = 150 \text{ Å.}$

*Ultra-violet light absorption of nitro-olefins in ethanol and n-hexane.*

	Ethanol.		n-Hexane.	
	$\lambda_{\max}$ , Å.	$\epsilon_{\max}$ .	$\lambda_{\max}$ , Å.	$\epsilon_{\max}$ .
CH <sub>2</sub> :CMe·NO <sub>2</sub> .....	2250	3,300	*	*
CHMe:CH·NO <sub>2</sub> .....	2290	9,400	2290	8,700
	2350	9,700		
CHMe:CMe·NO <sub>2</sub> .....	2340	5,600	2350	6,100
	2420	5,800		
	2500	5,600		
CMe <sub>2</sub> :CH·NO <sub>2</sub> .....	2450	8,600	2350	10,000
	2510	8,600		
CHPr $\beta$ :CMe·NO <sub>2</sub> .....	2420	6,000	2340	5,400
	2510	6,200	2420	5,600
	2580	6,000		
CHMe:CBr·NO <sub>2</sub> .....	2250	4,000	*	*
	2690	4,800		
CHMe:CH·CH:CH·NO <sub>2</sub> .....	2260	5,500	*	*
	2980	12,000		
CHPh:CH·NO <sub>2</sub> .....	2270	9,500	2230	10,300
	3090	16,500	2290	9,700
			2990	17,800
CHPh:CMe·NO <sub>2</sub> .....	2260	10,300	2230	9,500
	3050	12,400	2930	11,400
CHPh:C~Cl·NO <sub>2</sub> .....	2260	10,600	*	*
	3200	13,600		
CHPh:CBr·NO <sub>2</sub> .....	2260	8,700	*	*
	3240	12,000		

\* Not determined.

#### EXPERIMENTAL.

For the technique of the light absorption measurements, see Part I (*J.*, 1945, 490). The compounds examined had the following physical constants: 2-Nitroprop-1-ene, b. p. 68–70°/144 mm.,  $n_D^{20}$  1.4309; 1-nitroprop-1-ene, b. p. 45°/1.5 mm.,  $n_D^{19}$  1.4663 (Schmidt and Rutz, *Ber.*, 1928, **61**, 2142); 2-nitrobut-2-ene, b. p. 47–50°/9 mm.,  $n_D^{19}$  1.4616; 1-nitro-2-methylprop-1-ene, b. p. 48–49°/9.5 mm.,  $n_D^{17}$  1.4723 (Haitinger, *Annalen*, 1878, **193**, 368; *Monatsh.*, 1881, **2**, 286); 2-nitro-4-methylpent-2-ene, b. p. 67°/10 mm.,  $n_D^{19}$  1.4579; 1-bromo-1-nitroprop-1-ene, b. p. 59–60°/11 mm.,  $n_D^{17}$  1.5121; 1-nitropenta-1:3-diene, b. p. 78–79°/2.5 mm.,  $n_D^{19}$  1.5543;  $\beta$ -nitrostyrene, m. p. 57–58° (Worall, *Org. Synth.*, Coll. Vol. I, p. 413);  $\beta$ -nitro- $\beta$ -methylstyrene, m. p. 64°;  $\beta$ -chloro- $\beta$ -nitrostyrene, m. p. 48° (Priests, *Annalen*, 1884, **225**, 321);  $\beta$ -bromo- $\beta$ -nitrostyrene, m. p. 66° (Worall, *J. Amer. Chem. Soc.*, 1921, **43**, 919). They were prepared either according to the methods given in the references cited, or by methods which will be described in a separate publication. We are indebted to Drs. R. L. Heath and H. A. Figgott of I.C.I. Ltd., Dyestuffs Division, for a sample of 2-nitro-4-methylpent-2-ene.

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