371. *Researches on Acetylenic Compounds. Part XXXV.* The Influence of Propargylic Substituents on the Ultra-violet Absorption of Diacetylenes.*

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A number of 1 : 6-disubstituted derivatives of hexa-2 : 4-diyne have been prepared and their ultra-violet light-absorption properties have been examined. As compared with those of the parent hydrocarbon, they show progressive increases in both wave-length and intensity as the polarisability of the C–X bond increases; these shifts can be quantitatively correlated.

Preliminary examination of the light-absorption properties of conjugated diacetylenic compounds (see the previous paper) revealed an unusual dependence on the substituents attached to the carbon atoms adjacent to the chromophoric group. To make possible the more systematic investigation of this effect a series of functional derivatives of hexa-2 : 4-diyne-1 : 6-diol has been prepared. Advantage was taken of the fact that similar derivatives had already been prepared from but-2-yne-1 : 4-diol, and analogous methods in every case proved to be practicable. The compounds obtained (I; X = OMe, OAc, $O\cdot SO_2\cdot C_7H_7$, Cl, Br, I, NMe_2) were moderately stable, and all except the chloride and dimethyl ether crystallised; they were thus more suitable for spectrographic examination than most of the diacetylenic compounds described previously. Unfortunately attempts to prepare the corresponding methanesulphonate by the method used by Raphael and

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* Part XXXIV, preceding paper.

Sondheimer (*J.*, 1950, 2101) for non-2-yn-1-ol failed completely, as did several variants of their procedure; apparently hydrolysis of the product is more rapid than the acylation reaction by which it is formed.

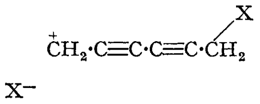
$XCH_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH_2X$ (I) $XCHMe{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CHMeX$ (II) $XCMe_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CMe_2X$ (III)

The ultra-violet light-absorption properties of the compounds obtained, together with that of (I; X = OH), are illustrated in Fig. 1. It is at once evident that these compounds have spectra resembling that of the parent hexa-2 : 4-diyne, but with shifts to lower frequency and higher intensity increasing in the order

$$(X =)\ H < OH, OMe < OAc < OTs < Cl < Br < I$$

(the anomalous case of the bisdimethylamino-compound is discussed below). These shifts are of considerable magnitude, and moreover appear to be related to each other. Fig. 2 shows a series of graphs, one for each maximum in the typical diyne spectrum, showing the relation between frequency and log $\varepsilon_{max.}$ for a range of substituents X; these are linear except that (I; X = OH) and (I; X = OMe) give points lying a little off the lines.

The decrease in frequency resulting from the substitution of X for hydrogen in the first (*i.e.*, lowest frequency) absorption maximum is a measure of the extent by which the substituent reduces the energy of the electronic transition responsible for absorption in this region. The increase in intensity is a measure of the distortion in the symmetrical π-electron system of the diacetylenic chromophore caused by the substituent, whereby the probability of the (forbidden) transition is increased. These two effects may both be ascribed to contributions from canonical forms of the types:



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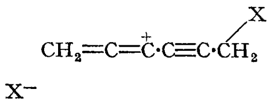

the importance of which is evident from the high chemical reactivity of the halides and toluene-*p*-sulphonate, reminiscent of allyl halides,* and more directly from the electron-diffraction results obtained by Pauling, Gordy, and Saylor (*J. Amer. Chem. Soc.*, 1942, **64**, 1753) for propargyl halides, which indicate an unusually long C–X bond. That they should be related to each other is not surprising, but such a relationship has not, so far as is known, been observed previously with any other group of similarly related compounds. From Fig. 2 it appears experimentally that the relationship is of the form

$$\Delta \log \varepsilon = k\Delta\bar{\nu}$$

Variochromic effects due to "allylic" (or "propargylic") substituents differ fundamentally from those observed when substituents possessing free electron-pairs are directly attached to unsaturated systems. Such allylic substituents might be described as hyperconjugative auxochromes, in contrast to the better-known conjugative auxochromes. Like the latter, they may be divided into two classes according to whether the substituent accepts a partial positive or negative charge; the familiar bathochromic effects of alkyl groups on the spectra of conjugated dienes (Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72) are evidence of positive hyperconjugation, while the effects discussed in this paper exemplify negative hyperconjugation. The latter phenomenon was first postulated by Baker (*J.*, 1939, 1155) and was invoked by de la Mare, Ingold, and Hughes to explain the difference in stability between the 1 : 2- and the 1 : 4-dibromide of butadiene (*J.*, 1948, 17). Unfortunately, few examples of compounds which might be expected to reveal spectrographic effects of this type have been examined; where the substituent is "allylic" rather than "propargylic" it is frequently difficult to be sure that the compound is free from its structural isomers. Nevertheless some scattered information is available—*e.g.*, regarding the poly-ω-chlorotoluenes (Hamner and Matson, *J. Amer. Chem. Soc.*, 1948,

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* Recent work by Hennion and Maloney (*J. Amer. Chem. Soc.*, 1951, **73**, 4735), however, suggests that this analogy is only partial.

70, 2482) and 1 : 6-dibromohexa-2 : 4-diene (Bateman, Cunneen, Fabian, and Koch, *J.*, 1950, 936). The most conspicuous cases of such interaction are the styrylcarbinols (*e.g.*, cinnamyl alcohol) studied by Braude and Timmons (*J.*, 1950, 2000), in which bathochromic and hyperchromic shifts ($\Delta\bar{\nu} = -880$ cm.$^{-1}$; $\Delta \log \varepsilon = +0{\cdot}211$) result from the introduction of a hydroxyl group into β-methylstyrene. During the preparation of the present paper Braude and Coles (*J.*, 1951, 2085) have made further observations in this field. Another example is the relationship between vitamin A and its acetate; in the latter the whole spectrum is shifted by about 12 Å ($\Delta\bar{\nu} = -160$ cm.$^{-1}$) to longer wave-lengths (Dr. H. B. Henbest, private communication). A more extensive range of substituents is available in the system $CH_3{\cdot}CHX{\cdot}CH{=}CH{\cdot}C{\equiv}CH$. (Table I). In every case bathochromic and hyperchromic displacements increase in the order X = H<OH<OAc<Cl<Br.

FIG. 1.

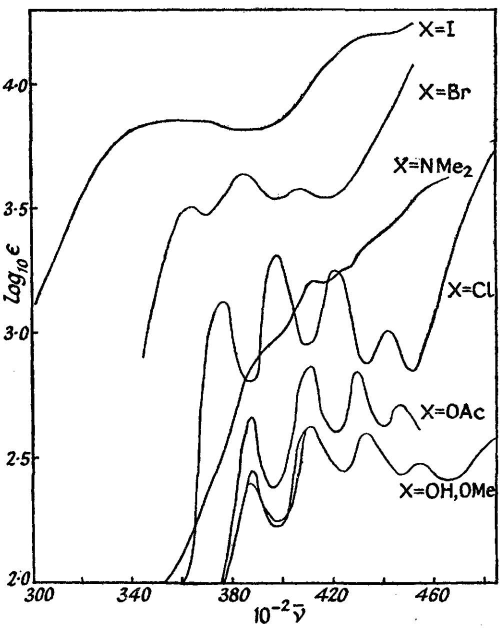
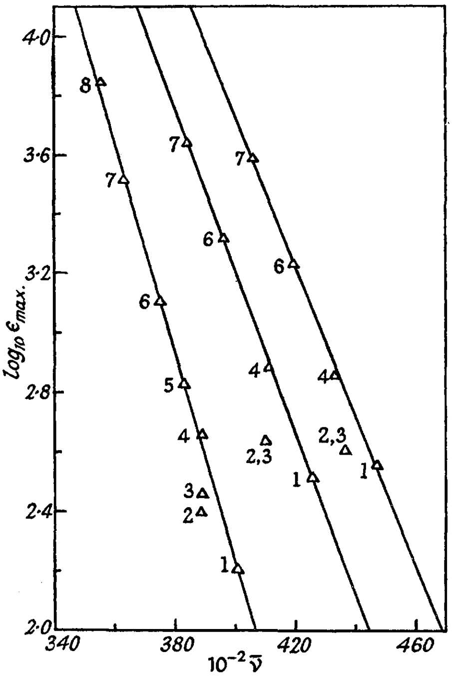


FIG. 2.



X	*No.*	X	*No.*
H	1	$O{\cdot}SO_2{\cdot}C_7H_7$	5
OH	2	Cl	6
OMe	3	Br	7
OAc	4	I	8

An alternative interpretation of these effects was suggested by the observation that 3-chloro- and 3-bromo-cholest-5-enes absorb much more intensely than cholest-5-ene itself in the 2100-Å region (Dr. H. B. Henbest, private communication). This must be due either to some effect peculiar to the rigid steroid nucleus, *e.g.*, to a modification of the steric strain inherent in ring B, or to a general tendency for polarisable substituents, not

TABLE 1. *Allylic substitution in vinylacetylenes.*

	$\lambda_{max.}$, Å	ε	λ, Å	ε
$CH_3{\cdot}CH{=}CH{\cdot}C{\equiv}CH$	2220	10,800	infl. 2285	8,000
$CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [1]	2230	13,000	infl. 2290	9,500
$CH_3{\cdot}CH(OMe){\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [2]	2235	12,500	infl. 2290	10,500
$CH_3{\cdot}CH(OAc){\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [3]	2235	13,000		
$CH_3{\cdot}CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [4]	2260	14,000		
$CH_3{\cdot}CHBr{\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [4]	2350	16,500		

[1] Jones and McCombie, *J.*, 1943, 261. [2] Heilbron, Jones, and Weedon, *J.*, 1945, 81. [3] Braude, *J.*, 1949, 794. [4] Henbest, Jones, and Walls, *J.*, 1950, 3646.

necessarily allylic, to modify the light-absorption properties of nearby unsaturated centres, which might be sufficient to account for the data discussed above.

$$XCH_2{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CH_2X \quad \text{(IV)}$$

The halides (IV; X = Cl and Br) were therefore prepared (as stable solids, by the action of lithium chloride and calcium bromide upon the corresponding ditoluene-*p*-sulphonate), and their light-absorption properties were determined. In Table 2 these are compared with those of related hydrocarbons and (IV; X = OH).

The effects of β-substituents are evidently of smaller magnitude than those of α-substituents; although some slight modifications, especially in the intensity of a forbidden transition, are to be expected when a polarisable substituent is introduced near an unsaturated centre, the pronounced variochromic effects discussed above are specific for the α-position, in which hyperconjugative interaction is possible.

It might be expected that if groups with a strong —*I* effect in the 1 and 6 positions of hexa-2 : 4-diyne reduce the energy of the electronic transition, then the substitution of methyl groups in the same positions should have the opposite effect. Such is apparently the case (Table 3) though, as again would be expected, the magnitude of the shift is small; fortunately the sharp bands permit the accurate measurement of the positions of the maxima.

In discussing the effects produced by various substituents it was pointed out that (I; X = NMe_2) was anomalous, giving a spectrum in which the characteristic fine structure had almost disappeared, while (I; X = OH and OMe) showed slight deviations from the

TABLE 2. 1 : 8-*Disubstituted derivatives of octa*-3 : 5-*diyne* (IV).

Compound	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε
	C		*B*		*A*	
(IV; X = H)	2275	360	2385	340	2530	230
(IV; X = Et)	2285	440	2395	390	2540	240
(IV; X = OH)	2285	450	2395	490	2540	330
(IV; X = Cl)	2290	440	2410	490	2550	280
(IV; X = Br)	2310	895	2420	895	2570	475

TABLE 3. *Comparison of diynes of types* I, II, *and* III.

(*a*) *Glycols.*

	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε
	C		*B*		*A*			
(I; X = OH)	2315	410	2440	440	2580	250		
(II; X = OH)	2320	320	2425	330	2560	210		
(III; X = OH)	2315	330	2420	365	2550	215		

(*b*) *Chlorides.*

	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε
	D		*C*		*B*		*A*	
(I; X = Cl)	2260	1080	2390	1810	2530	2090	2670	1360
(II; X = Cl) *	2270	1190	2380	1930	2520	2180	2660	1440
(III; X = Cl) *	2260	1210	2375	1750	2510	2090	2650	1330

* Forthcoming publication.

$\Delta \log \varepsilon = k\Delta\bar{\nu}$ relationship. While the cause of these anomalies is uncertain, it is perhaps significant that these are the only groups investigated which show strong +*T* effects, and that the dimethylamino-group with the strongest +*T* effect also shows the greatest spectroscopic anomaly.

The spacing of the vibrational fine structure in the spectra of the compounds (I) diminishes somewhat as the wave-length and intensity increase, indicating that substituents like chlorine reduce the energy of the symmetrical stretching vibration (A_1) of the diacetylene system in the excited state. The corresponding ground-state frequency in acetylenes is not markedly affected by such propargylic substituents (Wotiz, Miller, and Palchack, *J. Amer. Chem. Soc.*, 1950, **72**, 5055). In compounds (I; X = Br and I) this effect is partly spurious, being to some extent the result of the superposition of rising absorption attributable to an intense transition with $\lambda_{max.}$ below 2050 Å, and presumably analogous to the ultra-high-intensity bands of the higher poly-ynes discussed later (pp. 2012, 2015).

With (I; X = I) (but not the bromine analogue; see Fink and Goodeve, *Proc. Roy. Soc.*, 1937, *A*, **163**, 595) absorption by the iodine atoms affects the spectrum at shorter wavelengths.

EXPERIMENTAL

Absorption spectra were obtained with a Beckman DU or Unicam spectrometer, alcoholic solutions being used. In the case of (I; X = NMe_2) a 0·01% alcoholic sodium hydroxide solution was used. The maximum shown for (I; R = $O{\cdot}SO_2{\cdot}C_7H_7$) was obtained from a subtraction curve, by using ethyl toluene-*p*-sulphonate to eliminate the absorption of the aromatic groups; this could not be done below 2500 Å, where such absorption becomes too intense.

1 : 6-*Diacetoxyhexa*-2 : 4-*diyne*.—Hexa-2 : 4-diyne-1 : 6-diol (5·9 g.) was dissolved in dry pyridine (10 c.c.), and acetic anhydride (5·8 c.c.) was added with stirring at −5° during 15 minutes. The mixture was allowed to warm to room temperature, stirred overnight, and treated with water. The product was isolated with ether and fractionated to give 1 : 6-*diacetoxyhexa*-2 : 4-*diyne* (8·0 g., 80%) as an oil, b. p. 60° (bath temp.)/10^{-4} mm., n_D^{22} 1·5145, which crystallised on cooling; the solid had m. p. 14—16° (Found: C, 61·4; H, 5·4. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·2%).

1 : 6-*Dimethoxyhexa*-2 : 4-*diyne*.—Hexa-2 : 4-diyne-1 : 6-diol (2·0 g.) was stirred under nitrogen with a solution of sodium hydroxide (4·0 g.) in water (30 c.c.) while methyl sulphate (5·0 g.) was added dropwise during 3 hours. After 24 hours the product was isolated with ether and fractionated, giving 1 : 6-*dimethoxyhexa*-2 : 4-*diyne* (1·0 g., 40%), b. p. 60°/0·01 mm., n_D^{20} 1·5000 (Found: C, 69·1; H, 7·5. $C_8H_{10}O_2$ requires C, 69·5; H, 7·3%).

Hexa-2 : 4-*diyne*-1 : 6-*diol Ditoluene*-p-*sulphonate*.—Hexa-2 : 4-diyne-1 : 6-diol (6·9 g.) and toluene-*p*-sulphonyl chloride (28 g.) were dissolved in acetonitrile (50 c.c.), and the resultant solution was stirred and cooled while a solution of potassium hydroxide (7·0 g.) in water (12 c.c.) was added slowly during 15 minutes, the temperature being kept at 20—25°. The mixture was stirred overnight and then treated with water (75 c.c.) and ether (50 c.c.). The ethereal solution was washed with sodium hydrogen carbonate solution and water and dried. Removal of the solvent gave a syrup from which the product was obtained as a pink solid, m. p. 92—94°, by the addition of methanol (150 c.c.). The *ditoluene*-p-*sulphonate* (20·0 g., 77%), crystallised from methanol as large plates, m. p. 96°, which became pink on exposure to light (Found: C, 57·7; H, 4·6. $C_{20}H_{18}O_6S_2$ requires C, 57·4; H, 4·3%).

1 : 6-*Dichlorohexa*-2 : 4-*diyne*.—Hexa-2 : 4-diyne-1 : 6-diol (96 g.) was dissolved in dry pyridine (128 c.c.), and thionyl chloride (152 c.c.) was added dropwise during 3 hours with stirring and cooling, the temperature being kept at 10—20°. The mixture was allowed to warm to room temperature, stirred overnight, and treated with ice. The product was isolated with ether and fractionated to give 1 : 6-dichlorohexa-2 : 4-diyne (102 g., 80%), b. p. 54°/0·1 mm., n_D^{20} 1·5750 (Found: C, 49·3; H, 2·7. Calc. for $C_6H_4Cl_2$: C, 49·0; H, 2·7%) (Hunsmann, *Ber.*, 1950, **83**, 213, gives b. p. 65°/0·1 mm., n_D^{20} 1·5740). 1 : 6-Dichlorohexa-2 : 4-diyne has skin-irritant properties.

1 : 6-*Dibromohexa*-2 : 4-*diyne*.—(*a*) Calcium bromide (7·5 g.) was dissolved in dry ethanol (75 c.c.), and hexa-2 : 4-diyne-1 : 6-diol ditoluene-*p*-sulphonate (10·5 g.) was added. The mixture was refluxed for 15 minutes, and the product was isolated with ether, giving, after distillation, 1 : 6-*dibromohexa*-2 : 4-*diyne* (3·0 g., 50%), b. p. 100° (bath temp.)/0·01 mm., n_D^{20} 1·6432, which solidified on cooling; the solid had m. p. 16—18° (Found: C, 30·5; H, 1·9. $C_6H_4Br_2$ requires C, 30·5; H, 1·7%). 1 : 6-Dibromohexa-2 : 4-diyne is a powerful vesicant.

(*b*) Hexa-2 : 4-diyne-1 : 6-diol (5·9 g.) was suspended in benzene (40 c.c.) and phosphorus tribromide (13·7 g.) was added dropwise at room temperature with stirring; the stirring was continued overnight. Ice–water was added and the product isolated with ether to give 1 : 6-dibromohexa-2 : 4-diyne (8·3 g., 65%), b. p. 50° (bath temp.)/10^{-4} mm., n_D^{22} 1·6420.

1 : 6-*Di-iodohexa*-2 : 4-*diyne*.—Sodium iodide (5·0 g.) was dissolved in dry ethanol (50 c.c.), and hexa-2 : 4-diyne-1 : 6-diol ditoluene-*p*-sulphonate (4·5 g.) in dry chloroform (20 c.c.) was added, the mixture being kept in the dark for 24 hours. Water was then added and the product was isolated with ether and crystallised from light petroleum (b. p. 40—60°), giving 1 : 6-*di-iodohexa*-2 : 4-*diyne* (2·5 g., 71%) as pale yellow irregular plates, m. p. 64° (Found: C, 23·7, 23·5, 23·6; H, 1·8, 2·8, 1·2. $C_6H_4I_2$ requires C, 21·8; H, 1·2%).

1 : 6-*Bisdimethylaminohexa*-2 : 4-*diyne*.—(*a*) 1 : 6-Dibromohexa-2 : 4-diyne (2·6 g.) was slowly added with stirring at 20—30° to a solution of dimethylamine in water (25 c.c., 25%). The mixture was stirred for 18 hours and treated with water (50 c.c.); the product was isolated

with ether and fractionated to give 1 : 6-*bisdimethylaminohexa*-2 : 4-*diyne* (0·9 g., 50%), b. p. 65°/0·01 mm., n_D^{20} 1·5085, which solidified to give long plates, m. p. 28—29° (Found: C, 73·0; H, 9·7. $C_{10}H_{16}N_2$ requires C, 73·1; H, 9·8%). The *dipicrate* crystallised from ethanol as small prisms, m. p. 262° (Found: C, 42·7; H, 3·2. $C_{22}H_{22}O_{12}N_8$ requires C, 42·5; H, 3·6%).

(*b*) In a similar experiment the dichloride (I; X = Cl) (6·0 g.) gave a crude product which solidified and was crystallised from light petroleum (b. p. 40—60°), giving the diamine (3·0 g.), m. p. 29—30°.

Hydrogenation. When shaken with hydrogen in the presence of platinic oxide an uptake equivalent to 4·9 mols. was observed; addition of picric acid then resulted in the precipitation of dimethylamine picrate, m. p. and mixed m. p. 156°. Hydrogenolysis is frequently observed with acetylenic amines (Jones, Lacey, and Smith, *J.*, 1946, 940).

1 : 8-*Dichloro-octa*-3 : 5-*diyne*.—A solution of lithium chloride (17 g.) in 2-ethoxyethanol (150 c.c.) was dehydrated by distillation through an 8″ Dufton column until the boiling point reached 127°, and then cooled to 50° and treated with octa-3 : 5-diyne-1 : 8-diol ditoluene-*p*-sulphonate (45 g.; Cook, Jones, and Whiting, forthcoming publication). The mixture was refluxed for 15 minutes, cooled, and poured into water; extraction with ether gave a solution which was well washed with water, then dried (calcium chloride) in order to remove residual 2-ethoxyethanol. Evaporation gave a residue which solidified and was crystallised from aqueous ethanol, giving the *dichloride* (10 g., 57%) as prisms, m. p. 45° (Found: C, 54·8; H, 4·3; Cl, 40·8. $C_8H_8Cl_2$ requires C, 54·9; H, 4·6; Cl, 40·5%).

1 : 8-*Dibromo-octa*-3 : 5-*diyne*.—As prepared by the above method from the corresponding toluene-*p*-sulphonate (11 g.) and calcium bromide (10 g.) in 2-ethoxyethanol (100 c.c.), the *dibromide* (5·2 g., 80%) formed prisms, m. p. 65°, from methanol (Found: C, 36·5; H, 3·1. $C_8H_8Br_2$ requires C, 36·4; H, 3·05%).

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