

DIELS-ALDER ADDUCTS OF DICYANOACETYLENE AND THEIR ELECTRONIC SPECTRA

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Abstract—Dicyanoacetylene is a very reactive dienophile, forming Diels-Alder adducts with a wide variety of dienes, including durene. The UV spectra of the adducts include bands attributed to charge-transfer transitions with intensity borrowed from the local chromophores.

THE very strong electron withdrawal by the cyano-groups would be expected to make dicyanoacetylene more reactive than dimethyl acetylenedicarboxylate, a valuable and widely used dienophile. At the time this work was completed¹ only the reaction with cyclopentadiene² to form the adduct VIII had been reported. As a test of the acetylene's potency it was heated with durene at 150°. A low yield (5%) of a 1:1-adduct was produced, the structure of which VI was established by its absorption of three moles of hydrogen on catalytic reduction, and by its very simple PMR spectrum, consisting of only two singlets at τ 8.21 and 5.72 with relative intensities of 6:1. The unexpected bright yellow colour of the adduct and an interest in interaction between unconjugated chromophores led us to make a series of related compounds for spectral examination.

Dicyanoacetylene added rapidly to cyclohexadiene, cyclopentadiene and dimethylfulvene below room temperature to form the Diels-Alder adducts II, VIII and IX. The first took up one mole of hydrogen over Pd-CaCO₃, giving the compound I needed as a standard of the maleonitrile chromophore in the bicyclo[2.2.2]octane system unperturbed by other π -electrons. Although the dihydro derivative of the cyclopentadiene adduct has been reported,² we found no break in the speed of absorption of hydrogen and could isolate only the tetrahydro derivative X. At 100° naphthalene and anthracene gave the respective adducts IV and V in yields of about 30%. Hydrogenation of the naphthalene adduct could be controlled without difficulty to obtain the dihydro- III and tetrahydro derivative XI (or isomer). 2,6-Addition to bicyclo[2.2.1]heptadiene³ occurred in good yield at room temperature (VII).

The adducts II and V-VIII have been made independently by Weis.⁴

Since intramolecular charge-transfer seemed important in the spectrum of the durene adduct (VI), an attempt was made to obtain analogues with some of the Me groups replaced by the more strongly electron donating OMe groups. Diels-Alder addition to *o*-dimethoxybenzene might produce XII or XIII. The fraction of the mixture from reaction of dicyanoacetylene with veratrole at 150°, eluted from a silica column with benzene (corresponding with the fraction containing the yellow durene adduct), was coloured dark red, but could not be freed from unchanged veratrole without decomposition. The red colour may have been due to the adduct XII. A colourless, crystalline product separated in 6% yield was identified as the methoxy-

phthalonitrile (XIV), which must have arisen by elimination of methoxyacetylene from the other Diels–Alder adduct XIII. Similarly *m*-methoxytoluene gave a small amount of 3-methylphthalonitrile (XVI), evidently formed also by loss of methoxyacetylene from the initial adduct XV. The methoxymethylphthalonitrile that would have been formed by loss of acetylene was not isolated, nor were any of the four other substituted phthalonitriles that might have been formed by loss of one or other bridge from the two other possible Diels–Alder adducts, although they may have been present in small amounts.

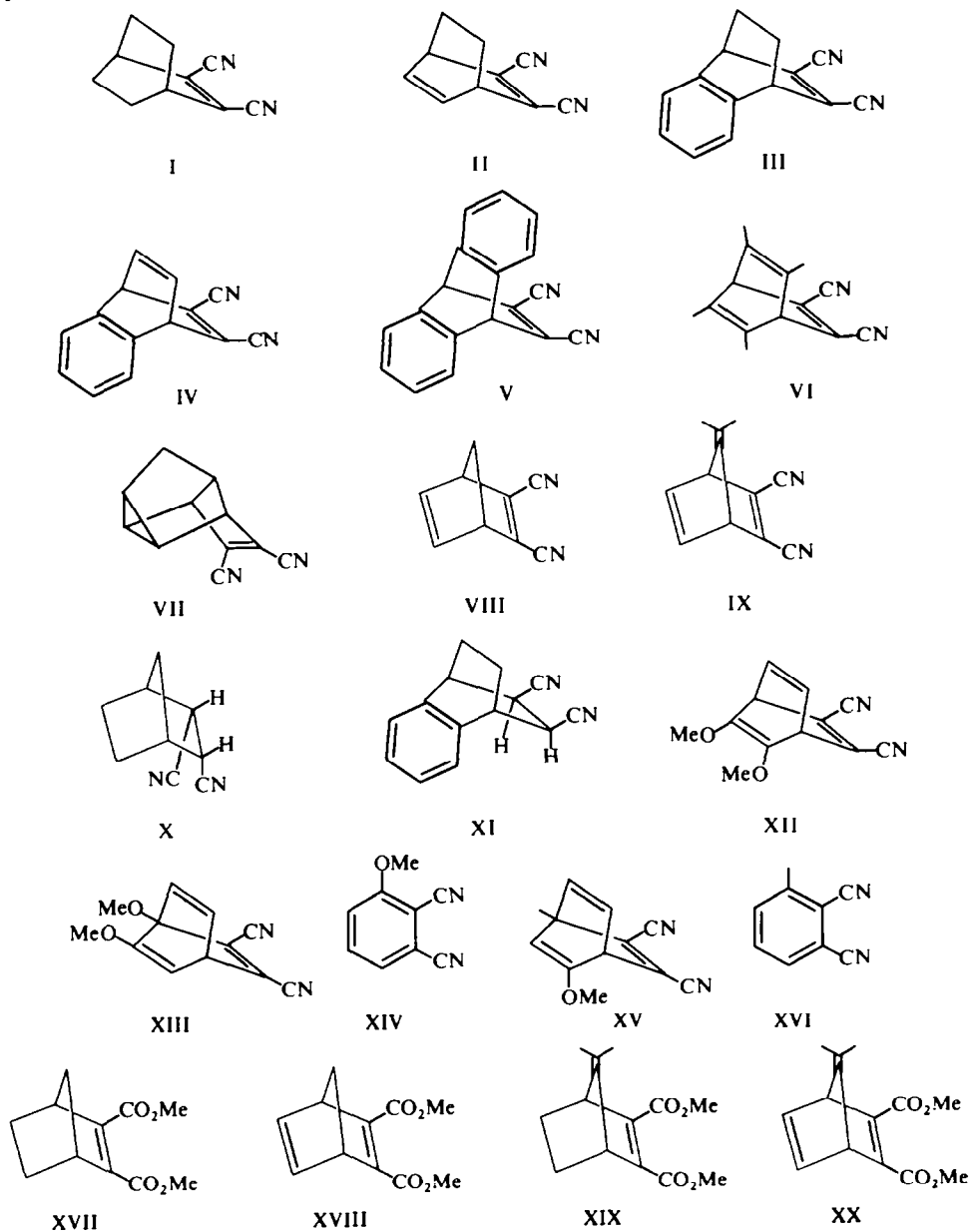


TABLE I. ABSORPTION SPECTRA IN ETHANOL

Compound	λ_{\max} (nm)	ϵ_{\max}	λ_{\max} (nm)	ϵ_{\max}	λ_{\max} (nm)	ϵ_{\max}
I	238	12,000				
II	237	8700	266*	700		
III	239	6700	267*	650		
			278**			
IV	233	6500	286*	830	313	760
V	233	7700	288**	780	314*	470
VI	242	5100	274*	750	361	250
VII	255	7900				
VIII	251	5300	291	610		
IX	245	5200	‡		331	500
XVII ¹¹	237	5700				
XVIII ¹¹	236	3900	280*	1200		
XIX ¹¹	231	6300	‡			
XX ¹¹	†		‡		308	870

* Shoulder.

** Includes benzenoid absorption.

† Strong broad band with no maximum above 220 nm.

‡ Band believed to be submerged under shorter wavelength absorption.

Electronic spectra

The UV spectrum of ethylene indicates allowed electronic transitions of 7.6 eV (163 nm band)⁵ and 6.4 eV (195 nm band).⁶ It is almost certain that the higher energy transition is singlet $\pi \rightarrow \pi^*$ (${}^1A_g \rightarrow {}^1B_{3u}$ in D_{2h} when the molecular axes are defined as in Fig. 1). The assignment of the other transition is much more doubtful but there is good evidence for singlet $\pi \rightarrow \sigma^*$ (${}^1A_g \rightarrow {}^1B_{1u}$).⁷

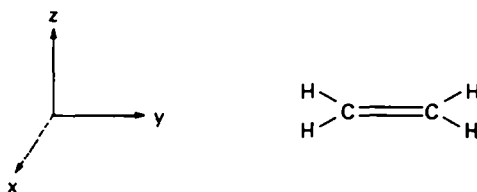


FIG. 1 Symmetry axes for ethylene.

In the dicyanoethylene chromophore the $\pi \rightarrow \pi^*$ transition has an energy lower than 7.6 eV. The corresponding spectral band occurs at 226 nm in maleonitrile,¹ at 247 nm in I and at 255 nm in VII. The band moves to longer wavelengths as the molecular strain increases. As no longer-wavelength absorption is discernable in any of the examples we assume that the $\pi \rightarrow \sigma^*$ band is buried under the stronger $\pi \rightarrow \pi^*$ absorption.

Norbornadiene may be regarded as a derivative of two ethylenic fragments. In order to interpret its spectrum we shall apply the procedure described by Murrell⁸ for analysing the UV spectrum of *cis*-butadiene, assuming that the behaviour of the π -electrons is independent of the structure of the σ -bond framework. From the data

of Robin *et al.*⁷ we calculate that the energies of the charge-resonance states are very close to the energy of a locally-excited ethylene state. Consequently of the first two excited states one should have a large charge-resonance character: the other should be an out-of-phase exciton state. Transitions from the ground state to these states should be respectively allowed and forbidden. The observed spectrum cannot be explained solely in terms of these transitions. It has been suggested⁹ that a $\pi \rightarrow \sigma^*$ transition is responsible for most of the intensity of the first observed band with the forbidden $\pi \rightarrow \pi^*$ transition providing an underlying absorption.

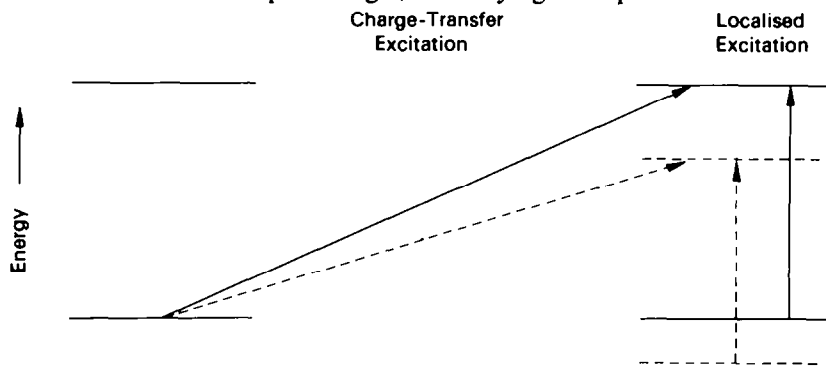


FIG. 2 Schematic representation of the electronic energy levels and excitation energies in non-conjugated dienes involving ethylene (————) and dicyanoethylene (-----) chromophores.

On replacing one of the ethylene chromophores with the dicyanoethylene chromophore the degeneracies in the zero-order states found in norbornadiene are removed. We can see from Fig. 2 that dicyanosubstitution must reduce the energy of the more stable charge-transfer state by an even greater amount than it reduces the energy of the ethylene $\pi \rightarrow \pi^*$ excited state.[†] In the spectrum of VIII we assign the first band as a predominantly $\pi \rightarrow \pi^*$ charge-transfer band and the second band as a characteristic dicyanoethylene band. We assume that the first $\pi \rightarrow \sigma^*$ band is buried under the stronger $\pi \rightarrow \pi^*$ absorption. A pure charge-transfer band would be forbidden, and the intensity of the first band may be regarded as having been borrowed from the dicyanoethylene band. The characteristic band of the dicyanoethylene chromophore loses intensity when a second double bond is introduced not only to the new charge-transfer band but also to the new ethylene chromophore band.

II differs from VIII in its σ -bond framework. Its spectrum strongly resembles that of VIII except that each of the transitions requires about one third of an electron volt more energy. The band separation is a little smaller and as a consequence the charge-transfer band appears only as a pronounced shoulder.

The only significant change in the spectrum of II when the ethylene chromophore is replaced by benzene (to give compound III) is the appearance of a long-wavelength shoulder characteristic of the aromatic chromophore. The charge-transfer band is not shifted because, although benzene is a better donor than ethylene, the remaining positive charge is more widely dispersed and therefore the coulombic stabilization of the charge-transfer state is reduced.

[†] In chloroform the intermolecular charge-transfer transition between maleonitrile and either cyclohexene or norbornene appeared at 265 nm. [Method of E. M. Kosower, *Trans. Farad. Soc.* **57**, 1662 (1961)].

The introduction of a second ethylene donor group into II must give rise to another zero-order charge-transfer state which is degenerate with the first one. The first-order states which result from linear combinations of the zero-order states are not degenerate because of the overlap of the two donor orbitals. Therefore we expect two charge-transfer bands at longer wavelengths than that of the dicyanoethylene band. This pattern should be found whenever there are two equivalent strong donors and is indeed observed in V and VI.* The splitting of the charge-transfer band is smaller in V than it is in VI because the overlap of the donor orbitals is smaller. The spectrum of V also contains long-wavelength aromatic absorption.

When the two donor groups are not equivalent the zero-order charge-transfer states are not in general degenerate. The factors responsible for the spectral similarities of II and III give rise to an accidental near degeneracy in IV. The spectrum of IV therefore strongly resembles that of V. In IX the donors differ from each other in their σ -bond framework and the coulombic stabilizations are not the same. The spectrum of IX resembles that of VIII and is quite different from that of VI. This suggests that the charge-transfer band which arises out of the introduction of the new olefinic group is buried under the dicyanoethylene band.

The charge-transfer bands should shift markedly on changing the polarity of the solvent. We observed blue shifts of more than 1000 cm^{-1} in the spectrum of VI on changing the solvent from ethanol to cyclohexane. The dicyanoethylene band, in contrast, suffered only a slight solvent shift.

The dimethyl maleate group is a weaker acceptor than the dicyanoethylene group. Therefore on replacing the CN groups in the compounds I to IX by COOMe groups blue shifts would be expected in all of the charge-transfer bands. Also the characteristic band of the dimethyl maleate chromophore lies at shorter wavelengths than that of the maleonitrile chromophore.¹⁰ The interpretation of the spectrum of XVIII suggested by Wilcox and Craig¹⁰ (i.e. a characteristic chromophore band at 235 nm with a long-wavelength inflection due to an underlying charge-transfer band) fits this pattern if the separation of the characteristic chromophore band and the charge-transfer band is smaller than in the spectrum of the analogous compound VIII. In the spectrum¹¹ of XX the low-energy charge-transfer band (corresponding to the 331 nm band of IX) is clearly visible.

EXPERIMENTAL

Dicyanoacetylene. An intimate mixture of acetylenedicarboxamide (7 g), dry sand (70 g) and P_2O_5 (35 g) was heated at 200° and a press of 2 mm of mercury in an apparatus similar to that described by Blomquist and Winslow.² The nitrile quickly distilled into the receiver, maintained at -80° , where it solidified to a white, crystalline solid (yield 29 to 40%).

2,3-Dicyanobicyclo[2.2.1]heptadiene (VIII). A soln of cyclopentadiene (10 ml) in light petroleum (20 ml) was cooled to -10° and added to freshly prepared dicyanoacetylene (1.4 g) also cooled to -10° . The mixture was further cooled for 10 min and then allowed to warm up for 1 hr. The solid remaining after evaporation to dryness was recrystallized from CHCl_3 -petroleum (60%), m.p. 44° (Lit.² $44-45^\circ$).

3-Methylphthalonitrile (XVI). Excess methyl *m*-cresyl ether (10 ml) and dicyanoacetylene (2.6 g) were heated together in a sealed tube at 150° for 15 hr. After cooling to room temp, the contents of the tube were extracted with EtOAc. The volume of the extract was reduced to 200 ml and benzene (400 ml) was added.

* As expected, the longest band moves to shorter wavelengths when the two dimethylethylene bridges in VI (λ_{max} 361 nm in ethanol) are progressively replaced by monomethylethylene (λ_{max} 339 nm in acetonitrile) and ethylene bridges (λ_{max} 315 nm in acetonitrile), in the adducts just described by E. Ciganek [*Tetrahedron Letters* 3321 (1967)].

Precipitated polymer was filtered off and the filtrate evaporated. The residue was chromatographed on silica gel. 50% benzene in petroleum eluted a fraction which contained unchanged ether and some yellow material. These could not be separated.

The benzene fraction gave XVI as a solid which was white after three recrystallizations from CHCl_3 -petroleum (4%), m.p. 139–140° (Lit. 143°). (Found: C, 76.3; H, 4.4; N, 19.3. Calc. for $\text{C}_9\text{H}_6\text{N}_2$: C, 76.0; H, 4.25; N, 19.7%). The PMR spectrum showed two peaks of equal intensity, one at τ 8.04 and one at 4.32. (*m*-Cyanotoluene has resonances at τ 8.20 and 4.37). These experiments employed the extreme sets of conditions for addition of dicyanoacetylene and all others were intermediate. To avoid repetition the other additions are, therefore, tabulated. (See Table 2).

TABLE 2.

Diene	Reaction conditions	Product	Yield	m.p.
Durene	sealed tube (b) 150°/12 hr	VI	5%	227–228°
Cyclohexa-1,3-diene	– 10°	II	54%	101°
Naphthalene	sealed tube (a) 100°/24 hr	IV	30%	155°
Dimethylfulvene	solution in petroleum – 10°	IX	37%	127–128°
Anthracene	sealed tube (a) 100°/3 hr	V	31%	265–266°
Bicyclo[2.2.1]heptadiene	room temp	VII	60%	84°
Veratrole	sealed tube (a) 150°/12 hr	XIV	6%	178–179°

Chromatography on silica gel—obtained by eluting (a) with 5% ethyl acetate in benzene, or (b) with benzene.

All products were recrystallized from chloroform/petroleum. Analyses are as given in Table 3.

TABLE 3.

	% Found				% Required		
	C	H	N		C	H	N
VI	79.9	6.6	13.6	$\text{C}_{14}\text{H}_{14}\text{N}_2$	80.0	6.7	13.3
II	76.9	5.35	18.15	$\text{C}_{10}\text{H}_8\text{N}_2$	76.9	5.2	17.9
IV	82.3	4.0	14.0	$\text{C}_{14}\text{H}_8\text{N}_2$	82.3	3.95	13.7
IX	79.4	5.6	14.9	$\text{C}_{12}\text{H}_{10}\text{N}_2$	79.1	5.5	15.4
V	84.85	3.85	11.35	$\text{C}_{18}\text{H}_{10}\text{N}_2$	85.0	4.0	11.0
VII	78.8	4.9	16.2	$\text{C}_{11}\text{H}_8\text{N}_2$	78.55	4.8	16.7
XIV	66.9	3.9	17.7	$\text{C}_9\text{H}_6\text{N}_2\text{O}$	68.35	3.8	17.7

Hydrogenation of 5,6,7,8-tetramethylbicyclo[2.2.2]octadiene-2,3-dinitrile (VI). When the adduct VI (11 mg) was hydrogenated in EtOAc over 5% Pd-C in a micro-hydrogenator, hydrogen (3.34 ml) was absorbed, equiv to 2.85 moles H_2 /mole of adduct, and the yellow colour disappeared.

2,3-Dicyanobicyclo[2.2.2]oct-2-ene (I). The corresponding II (625 mg) was hydrogenated in EtOAc over 5% Pd-CaCO₃. Absorption of H_2 was stopped after uptake of approximately one molecular proportion (90 ml) and the H_2 atmosphere quickly drawn off. The product was recrystallized from CHCl_3 -petroleum (85%), m.p. 119–120°. (Found: C, 75.6; H, 6.3; N, 18.0. $\text{C}_{10}\text{H}_{10}\text{N}_2$ requires: C, 75.9; H, 6.4; N, 17.7%.)

Hydrogenation of 5,6-benzobicyclo[2.2.2]octatriene-2,3-dinitrile (IV). The adduct IV (500 mg) was hydrogenated in EtOAc over 5% Pd-CaCO₃. Absorption of H_2 was stopped after uptake of approximately one molecular proportion, and the product was recrystallized from CHCl_3 -petroleum (87%), m.p. 154–155°.

mixed m.p. with starting material 119–137°. (Found: C, 81.5; H, 4.9; N, 13.6. $C_{14}H_{10}N_2$ requires: C, 81.5; H, 4.9; N, 13.6%.) The same adduct was also fully hydrogenated under the same conditions, m.p. 273–275°. (Found: C, 80.15; H, 5.8; N, 13.85. $C_{14}H_{12}N_2$ requires: C, 80.7; H, 5.8; N, 13.45%.)

Addition of dicyanoacetylene to cyclo-octatetraene. Cyclo-octatetraene (5 ml) and dicyanoacetylene (1.3 g) were heated together in a sealed tube at 100° for 4 hr. The contents of the tube were chromatographed on silica gel.

The benzene fraction gave a white solid adduct which was recrystallized from $CHCl_3$ -petroleum (34%), m.p. 140°. (Found: C, 80.3; H, 4.5; N, 15.6. $C_{12}H_8N_2$ requires: C, 80.0; H, 4.5; N, 15.6%.)

5% EtOAc in benzene eluted a gummy solid (29%), part of which was sublimed for analysis, m.p. 175°. (Found: C, 80.7; H, 3.5; N, 15.9. $C_{12}H_8N_2$ requires: C, 80.9; H, 3.4; N, 15.7%.)

Hydrolysis of veratrol product. The dinitrile XIV (350 mg) in wet EtOH (50 ml) and conc H_2SO_4 (12 ml) was refluxed for a week. Water (50 ml) was added and the EtOH distilled off. Extraction with $CHCl_3$ yielded a gum, which was refluxed with 20% NaOH aq (50 ml) for 4 hr, acidified and extracted with $CHCl_3$ (3 × 50 ml). The combined extracts were dried (Na_2SO_4) and the resulting diacid recrystallized from $CHCl_3$ -petroleum (21%), m.p. 174–175°. (Found: C, 54.5; H, 4.1, O, 41.0. $C_9H_8O_3$ requires: C, 55.1; H, 4.1; O, 40.8%.)

Intermolecular charge-transfer spectra. Several spectra were run of cyclohexene in $CHCl_3$. The cyclohexene concentrations were 1,2,4,8 drops in a 1 cm cell of solvent. A $\frac{1}{2}$ molar soln of maleonitrile, in $CHCl_3$, was then placed in sample and reference cells and a base line run. Several spectra were then run with 1,2,4,8 drops cyclohexene added to the sample cell and the same volume of solvent added to the reference cell.

The former procedure showed the end-absorption of the donor and subtraction of this from the spectrum obtained with maleonitrile present gave the absorption of the complex. A similar procedure was adopted with norbornene.

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