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DICYANOACETYLENE ADDUCTS AND THEIR ELECTRONIC SPECTRA

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WE wish to draw attention to the powerful dienophilic properties of dicyanoacetylene[1] and to the unusual absorption spectra of some of its adducts. Thus it reacts with simple dienes like cyclopentadiene[1] and cyclohexa-1,3-diene below room temperature to give the expected adducts (VII and II). As well as adding readily to anthracene (to give V) dicyanoacetylene reacts below 150° (when it begins to decompose) with naphthalene and with durene forming the adducts IV and VI. The structure of the durene adduct follows from its proton magnetic resonance spectrum, which shows only two sharp lines at 5.7 and 8.2 τ with the approximate intensities of 1 and 6. Adducts from other benzene derivatives have been prepared, but in some cases they cannot be isolated because of elimination of another acetylene to give a substituted phthalonitrile. For comparison, bis-trifluoromethylacetylene is reported[2] to add to durene at 200°.

Bicyclo[2,2,1]heptadiene reacts[3] at room temperature to give the adduct (VIII) in high yield. (The analogous reaction with bis-trifluoromethylacetylene proceeds[2] at 150°.)

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[1] A.T. Blomquist and E.C. Winslow, J. Org. Chem. 10, 149 (1945).

[2] C.G. Krespan, B.C. McKusick and T.L. Cairns, J. Amer. Chem. Soc. 83, 3428 (1961).

[3] Cf. E.F. Ullman, Chem. & Ind. 1173 (1958); A.T. Blomquist and Y.C. Meinwald, J. Amer. Chem. Soc. 81, 667 (1959); H.K. Hall, J. Org. Chem. 25, 42 (1960); R.C. Cookson, S.S.H. Gilani and I.D.R. Stevens, Tetrahedron Letters 615 (1962).

TABLE 1

Absorption Spectra in Ethanol

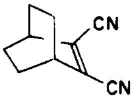
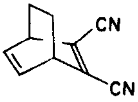
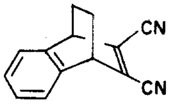
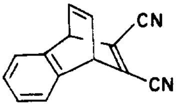
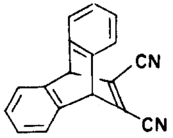
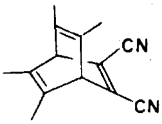
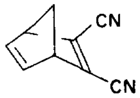
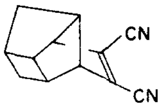
Compound		λ_{max} in mμ* (ε below)		
I		238(247)mμ 12,000	-	-
II		237(244) 8700	266 mμ 700	-
III		239(246) 6700	(267 & 278) 650	-
IV		233(242) 6500	286 830	313 mμ 760
V		233(244) 7700	288 780	314 470
VI		242(250) 5100	274 750	361 250

TABLE 1 (Continued)

Compound		λ_{max} in m * (ε below)		
VII	 CN CN	251(261) 5300	291 610	-
VIII	 CN CN	255 7900	-	-

* Inflections in parentheses.

The most striking property of the durene adduct is its bright yellow colour. Examination of the spectra of related compounds (see Table 1) suggests a possible reason for this rather unexpected colour. Dicyanobicyclo[2,2,2]octenes and [2,2,1]heptenes with no other unsaturation show only a single intense maximum due to the maleonitrile chromophore, at substantially longer wavelengths in the latter because of increased strain.[4] Introduction of a second double bond into another [2] bridge reduces the intensity of the main band (compare I and II) and produces a new one at longer wavelength. The phenomenon, which has often been observed before in analogous acids and ketones,[5] can be attributed to orbital overlap, the new band being associated with the transfer of an electron from an orbital resembling the π-orbital of the unperturbed double bond to one resembling the lowest empty orbital of the maleonitrile group (a better acceptor than acid or ketone,[5] so leading to absorption at longer wavelength). Presumably

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[4] *Cf*. W.M. Schubert and W.A. Sweeney, *J. Amer. Chem. Soc.* **77**, 2297 (1955); and ref. 5.

[5] E.R.H. Jones, G.H. Mansfield and M.C. Whiting, *J. Chem. Soc.* 4073 (1956), and references given therein.

a benzene ring can act in the same way as a double bond, although the charge-transfer band then overlaps the aromatic absorption.[6] There is little sign of charge-transfer from the cyclopropane ring in VIII, even though symmetry might allow it:[7] the charge-transfer absorption may be buried under the main band.

Introduction of a second donor group in IV, V and VI leads to the appearance of yet a third band. We attribute this to the splitting of the charge-transfer transition because of the two overlapping donor orbitals' being either in or out of phase. The larger splitting in VI than in IV or V arises from the greater overlap of the more compact olefinic orbitals than of the more extensive and divergent benzene orbitals.

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[6] Cf. H. Birnbaum, R.C. Cookson and N. Lewin, J. Chem. Soc. 1224 (1961).

[7] C.F. Wilcox and R.R. Craig, J. Amer. Chem. Soc. 83, 4258 (1961).