similarity between the findings with the hormones and observations with S-peptide. Large portions of S-peptide can be removed without destroying its function and small subunits (peptide IV), when employed in high enough concentrations, generate enzymic activity. The "active site" of S-peptide appears to be located in the peptide phenylalanylglutamylarginylglutaminylhistidine. The rest of the molecule, particularly the glutamic acid residue in the N-terminal end and the sequence methionylaspartylserine, provides important "binding sites." Histidine must play a key role in catalysis; the involvement in catalytic function of the other amino acid residues located within the "active site" of S-peptide remains to be established.

Communications to the Editor

On the Optical Absorptions of Phthalocyanines

Sir:

In the course of our investigations of dyes as saturable absorbers for use in laser Q-switching, we have remeasured the optical absorption and fluorescence spectra of phthalocyanine solutions. In this note, we wish to compare the spectra of both the metal-free (H_2Pc) and copper (CuPc) derivatives and report on extra absorption and emission bands observed for these complexes. Pure phthalocyanine single crystals were ground into powder and dissolved in 1-chloronaphthalene to yield 10^{-5} *M* solutions. Each solution was examined visually by passing an intense beam of light through it. Colloidal particles were discovered in the solutions, indicating that we do not have a true solution but rather a mixture of a true solution and a small amount of solid phase. Consequently, the given amplitudes of the extinction coefficient are lower limits.

The spectral absorption curves were measured at room temperature with a Cary Model 14R recording spectrometer. Beckman absorption cells of 5-cm. and 10-cm. path length were used. An absorption spectrum for the 1-chloronaphthalene solvent recorded in the spectral region of interest revealed one strong band at 3450 Å. and therefore limited our measurements in the ultraviolet region. The absorption spectra of H_2Pc and CuPc are shown in Figure 1, and the pertinent data are listed in Table I. The fluorescence emission spectrum (Figure 2) for H_2Pc dissolved in 1-chloronaphthalene was recorded at 77°K. by passing the spectral output through a Bausch and Lomb grating monochromator to a photomultiplier detector (RCA 7102-Sl) and electrometer, the output of which was automatically recorded. The fluorescence bands were observed at 6990, 7350, and 7775 Å., respectively.

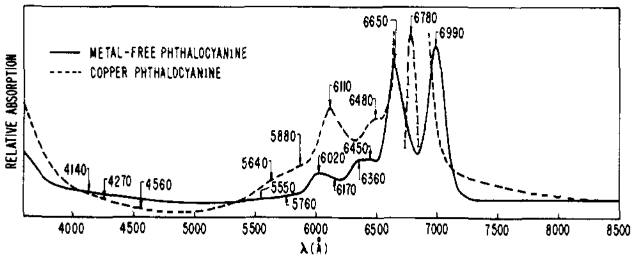


Figure 1. Absorption spectra of phthalocyanines in 1-chloronaphthalene.

Table I. Wave Length and Extinction Coefficient of Absorption Bands

	H_2Pc		CuPc	
	λ_{max}, Å.	log ε	λ_{max}, Å.	log ε
a	6990	4.23	6780	5.1
b	6650	4.19	6480	4.36
c	6450	3.71	6110	4.39
d	6360	3.71	5880	3.57
e	6170	3.44	5640	3.37
f	6020	3.54	4560	2.38
g	5760	2.89	4270	3.0
h	5550	2.59	4140	3.69

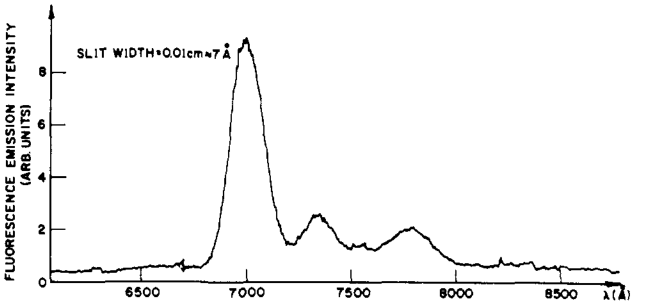


Figure 2. Fluorescence emission spectrum of metal-free phthalocyanine.

In the absorption spectra, no peaks in the ultraviolet due to the absorption of the 1-chloronaphthalene are listed here. However, ultraviolet measurements of thin films of H_2Pc gave peaks at 3334 and 2892 Å., while CuPc has peaks at 3292 and 2613 Å. The absorptions a through e in CuPc have been observed in the spectra recorded recently by Whalley,[1] which are considered to be more accurate than those reported previously. The H_2Pc spectrum is shown here to have eight distinct absorption maxima in the region 5500–7000 Å., while that of CuPc has five. Previously unrecorded absorptions at 6360 and 6170 Å. were observed. Although in Figure 1 these additional bands and others appear to be weak and therefore doubtful,

(1) M. Whalley, *J. Chem. Soc.*, 866 (1961).

we should point out that for the sake of reporting the complete absorption spectrum in a reasonable scale we have considerably decreased the intensities of the bands in Figure 1. The additional peaks are, however, clearly resolved if one uses either the 5- or 10-cm. absorption cell. Three additional lines that were not seen in the H_2Pc spectrum were recorded in the CuPc spectrum at 4560, 4270, and 4140 Å.

The CuPc molecule has D_{4h} symmetry, while the molecular symmetry of the H_2Pc is only D_{2h}. According to Lyons and co-workers,[2] one can tentatively describe the two bands a and b in H_2Pc as components of an electronic transition which in CuPc (D_{4h}) would be terminated by a degenerate level. Note, however, that the separation between the first pair of peaks (a and b) in H_2Pc is approximately three times the separation of the second pair (c and d) and twice that of the third pair (e and f). If one assumes that each pair is a split doublet, this implies that a different doublet orbital is involved in each transition. In an LCAO calculation,[3] the amount of splitting will be proportional to the square of the coefficients of the p_z-orbitals of the four adjacent nitrogens.

The intense fluorescence band at 6990 Å. in H_2Pc coincides with the first absorption band which is assumed to correspond to the first excited electronic level in the molecule. According to Kasha,[4] transitions involving emission in a condensed organic molecule always take place from the lowest excited electronic level independently of the order of levels to which the molecule was excited upon absorption of light. The two weaker fluorescence bands at 7350 and 7775 Å. can therefore be interpreted as vibrational levels characteristic of the molecular ground state. The separation between these bands is of the order of 740 cm.$^{-1}$. Indeed, infrared spectra[5] of phthalocyanines have revealed a strong common vibrational band at about 750 cm.$^{-1}$ which supports the interpretation that the additional bands in the fluorescence spectrum are vibrational in origin.

(2) L. E. Lyons, J. R. Walsh, and J. W. White, *J. Chem. Soc.*, 167 (1960).

(3) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(4) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

(5) A. N. Sidorov and I. P. Kotlyar, *Opt. Spectry.* (USSR), **11**, 92 (1961).

J. M. Assour, S. E. Harrison
RCA Laboratories
Princeton, New Jersey

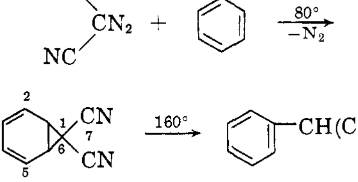
Received November 6, 1964

7,7-Dicyanonorcaradienes

Sir:

Rigorous evidence for the existence of simple norcaradiene derivatives, as pure compounds or in equilibrium mixtures with their valence-tautomeric cycloheptatrienes, has not been presented to date.[1] Stable norcaradienes have only been obtained by bridging C-1 and C-6 with a three-atom bridge[2] or by incorporating one or both double bonds into an aromatic system.[3] We now wish to report that the adducts of dicyanocarbene to benzene and *p*-xylene exist in the norcaradiene form.

Reaction of dibromomalononitrile with hydrazine in tetrahydrofuran at −70° gave carbonyl cyanide hydrazone[4] in 30–40% yield, m.p. 122–124° dec., λ_{max}^{MeCN} 282 mμ (ε 13,500), broad singlet at τ 0.65 in the n.m.r. spectrum. Oxidation of the hydrazone with lead tetraacetate in acetonitrile furnished dicyanodiazomethane in almost quantitative yield as a highly explosive, pale yellow solid, λ_{max}^{MeCN} mμ (ε) 241 (12,400), 313 (107), and 370 (shoulder, 50); ν_{max} (KBr pellet, cm.$^{-1}$) 2225, 2140, 1240, and 1215; the triphenylphosphine adduct melts at 171–173° dec. Thermolysis or photolysis of dicyanodiazomethane in benzene gave 7,7-dicyanonorcaradiene (**1**, 80% yield) as a colorless solid, m.p. 98.0–98.5°, which on heating to 160° rearranged to phenylmalononitrile. The n.m.r. spectrum of **1** in $CDCl_3$ shows four olefinic protons at τ 3.2–3.8 and a triplet, split further, and centered at τ 6.53, assigned to the protons on C-1 and C-6. Although this value is rather low for protons on a cyclopropane ring, it is readily explained by the combined deshielding effects of two cyano groups[5] and two double bonds. By comparison, the protons on C-1 and C-6 in 7-cyanocycloheptatriene (**2**)[6] absorb at τ 4.67. The ultraviolet spectrum of **1** ($\lambda_{max}^{cyclohexane}$ 271 mμ (ε 2920)) is that expected for the norcaradiene chromophore[7] and is different from that of 7-cyanocycloheptatriene (λ_{max} 255 mμ (ε 3710)).[6]



1

Hydrogenation of 7,7-dicyanonorcaradiene over palladium resulted largely in the reduction of the cyano groups, but cyclohexylmalononitrile could be isolated in 10% yield; this product is believed to have arisen by hydrogenolysis of the cyclopropane ring followed by saturation of the double bonds. Hydrolysis of **1** with alkaline hydrogen peroxide afforded 7-cyano-7-carbamidonorcaradiene, m.p. 155° (protons on C-1 and C-6 as a triplet centered at τ 7.25 in the n.m.r. spectrum), which on catalytic hydrogenation gave α-cyanocyclohexylacetamide in 40% yield.

Thermolysis of dicyanodiazomethane in *p*-xylene furnished a mixture of 2,5-dimethyl-7,7-dicyanonor-

---

(1) For a recent review of the cycloheptatriene–norcaradiene problem, see S. J. Rhoads in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 700–703; *cf.* also F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(2) (a) J. Schreiber, W. Leimgruber, M. Pesaro, P. Schudel, T. Threlfall, and A. Eschenmoser, *Helv. Chim. Acta*, **44**, 540 (1961); (b) R. Darms, T. Threlfall, M. Pesaro, and A. Eschenmoser, *ibid.*, **46**, 2893 (1963); (c) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963); *cf.*, however, L. H. Knox, E. Velarde, and A. D. Cross, *J. Am. Chem. Soc.*, **85**, 2533 (1963).

(3) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959); R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961); M. J. S. Dewar and C. R. Ganellin, *J. Chem. Soc.*, 3139 (1959).

(4) This reaction was first carried out by Dr. T. H. Regan of the explosives department. All new compounds reported gave satisfactory carbon, hydrogen, nitrogen, and molecular weight analyses.

(5) Such an effect in the n.m.r. spectra of polycyanocyclopropanes was recently noted by H. Hart and F. Freeman, *J. Org. Chem.*, **28**, 1220 (1963).

(6) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

(7) The anhydride of norcaradiene-1,6-dicarboxylic acid[2b] has a maximum at 269 mμ (ε 2300 in isooctane); tricyclo[4.3.1.$0^{1,6}$]deca-2,4-diene[2c] absorbs at 273 mμ (ε 2900).