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.

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[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).

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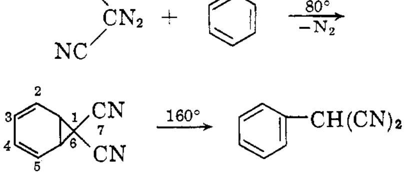
7,7-Dicyanonorcaradienes

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., $\lambda_{\max}^{\mathrm{MeCN}}$ 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, $\lambda_{\max}^{\mathrm{MeCN}}$ mμ (ϵ) 241 (12,400), 313 (107), and 370 (shoulder, 50); $\nu_{\max}$ (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** ($\lambda_{\max}^{\mathrm{cyclohexane}}$ 271 mμ (ϵ 2920)) is that expected for the norcaradiene chromophore[7] and is different from that of 7-cyanocycloheptatriene ($\lambda_{\max}$ 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-

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[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).

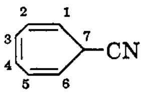
[4] This reaction was first carried out by Dr. T. H. Regan of the explosives department. All new compounds reported gave satisfactory carbon, hydrogen, nitrogen, and molecular weight analyses.

[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).

caradiene (**3**, 41% yield) and 1,4-dimethyl-7,7-dicyanonorcaradiene (**4**, 39% yield). Isomer **3**, m.p. 123–124°, absorbs at 279 mμ (ϵ 4900) and 238 mμ (ϵ 3290) in the ultraviolet spectrum; its n.m.r. spectrum shows singlets at τ 7.87 (methyl groups), 6.78 (protons on C-1 and C-6), and 3.81 (olefinic protons). The second isomer, **4**, was obtained in only 90% purity, m.p. 91–95°, $\lambda_{\max}$ 276 mμ (ϵ 2540) and 235 mμ (shoulder, ϵ 1850). Its n.m.r. spectrum exhibits a singlet at τ 8.27 (C-1 methyl), a doublet (J = 1 c.p.s.) centered at 7.97 (C-4 methyl), a doublet ($J_{5,6}$ = 6 c.p.s.) centered at 6.88 (proton on C-6), and the olefinic protons as an AB quartet (doublet components centered at τ 3.63 and 3.96, $J_{2,3}$ = 10 c.p.s.; protons on C-2 and C-3) superimposed on further bands (proton on C-5). Both isomers rearranged on heating to 2,5-xylylmalononitrile, m.p. 56–58°, which was degraded to 2,5-xylylacetic acid by acid-catalyzed hydrolysis and decarboxylation.



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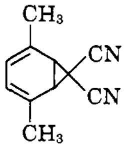

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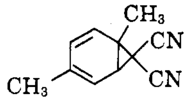
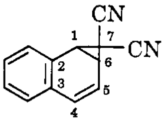


4

Thermal decomposition of dicyanodiazomethane in naphthalene resulted in the formation of three isomers of $C_{13}H_8N_2$, assigned structures **5**, **6**, and **7** on the basis of spectral evidence. The main product 7,7-dicyano-2,3-benzonorcaradiene (**5**, m.p. 126–127°), obtained in 50% yield, shows maxima at 227 mμ (ϵ 25,200) and 272 mμ (ϵ 7900) in the ultraviolet spectrum. Its n.m.r. spectrum displays the aromatic protons as a multiplet at τ 2.2–2.7, the olefinic protons as a doublet centered at 3.03 and a quartet centered at 3.77 ($J_{4,5}$ = 10 c.p.s.), the proton on C-1 as a doublet centered at 6.20, and the proton at C-6 as a quartet centered at 6.65 ($J_{1,6}$ = 9 c.p.s.). The mixture of **6** and **7** was isolated in 12% yield. The ultraviolet spectrum of 7,7-dicyano-1,2-benzocyclohepta-1,3,5-triene (**6**, m.p. 87–88°; $\lambda_{\max}$ 277 mμ (ϵ 8000); $\lambda_{\min}$ 243 mμ (ϵ 2600)) is almost superimposable on that of 1,2-benzocyclohepta-1,3,5-triene[8] ($\lambda_{\max}$ 275 mμ (ϵ 7400); $\lambda_{\min}$ 243 mμ (ϵ 2900)). The n.m.r. spectrum of **6** shows only aromatic and olefinic protons, the highest-field signal being a doublet centered at τ 4.12, probably due to the proton adjacent to the dicyanomethylene group. The ultraviolet spectrum of 7,7-dicyano-3,4-benzocyclohepta-1,3,5-triene (**7**, m.p. 85–90°, $\lambda_{\max}$ 228 mμ (ϵ 45,700) and 257 mμ (ϵ 5900)) is again almost identical with that of the parent 3,4-benzocyclohepta-1,3,5-triene[8] ($\lambda_{\max}$ 228 mμ (ϵ 44,000) with a shoulder at 256 mμ (ϵ 5200)). The n.m.r. spectrum of **7** shows the aromatic protons as a barely split singlet at τ 2.39 and the olefinic protons as two doublets centered at 2.89 and 3.93, respectively ($J_{1,2}$ = 10 c.p.s.). The two dicyanobenzocycloheptatrienes **6** and **7** probably were formed by the addition of dicyanocarbene to the 1,9 and 2,3 bonds of naphthalene, followed by rearrangement of the *o*-quinonoid norcaradienes to the more stable benzocycloheptatrienes.[9] To our knowledge this represents the first example of a carbene addition to bonds other than the 1,2 bond in naphthalene.



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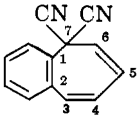

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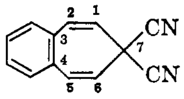

7

The isomers **5**, **6**, and **7** provide good models for the 7,7-dicyanonorcaradiene and 7,7-dicyanocycloheptatriene systems. The n.m.r. spectra of **6** and **7** show that the protons on C-1 and C-6 in the hypothetical 7,7-dicyanocycloheptatriene would be expected to absorb at *ca.* τ 4, whereas these signals in **1**, **3**, and **4** actually occur at τ 6.5 to 7, as predicted on the basis of the spectrum of **5**. Solubility difficulties prevented the determination of the n.m.r. spectrum of **1** at temperatures below −70°, so that the possibility cannot be excluded that in solution **1** is in equilibrium with a small amount of the valence-tautomeric 7,7-dicyanocycloheptatriene. Structure determination by X-ray diffraction[10] corroborates the assignment of the norcaradiene structure to crystalline **3**.

Details of these and other reactions of dicyanodiazomethane will be reported shortly.

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(8) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

(9) The adduct of dicyanocarbene to the 9,10 bond of naphthalene could not be found among the products. If formed at all, it may have rearranged to **6** during the isolation procedures; such a rearrangement has been observed in the case of the related 1,6-oxido[10]annulene [E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *Angew. Chem.*, **76**, 785 (1964); F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964)].

(10) C. J. Fritchie, to be published.

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Photoinduced Nucleophilic Substitution in Polyhedral Boranes

Sir:

The polyhalogenated derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are remarkably inert toward nucleophiles.[1] They are, however, photolytically unstable and easily undergo photoinduced nucleophilic substitution when irradiated in the presence of a suitable anion. This reaction, unprecedented in boron chemistry,[2] makes it possible to prepare many hitherto inaccessible polyhedral boranes and is the subject of this communication.

When an aqueous solution 0.07 *M* in $B_{12}Br_{12}^{2-}$ and 1.7 *M* in potassium cyanide was irradiated with a low-pressure mercury lamp for 4 days at room temperature, a 56% yield of $B_{12}Br_3(CN)_9^{2-}$, precipitated as the cesium salt, was obtained. The structure assignment rests on analysis (*Anal.* Calcd. for $C_9B_{12}Br_3Cs_2N_9\cdot H_2O$:

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(1) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

(2) Some analogy for it may be found in photochemical solvolyses of nitrophenyl phosphates and sulfates [E. Havinga, R. O. de Jongh, and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956)], benzylic chlorides and acetates [H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963)], nitrophenyl trityl ethers [H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963)], as well as the photoinduced displacement of nitrite ion from various aromatic nitro compounds by hydroxide ion or pyridine [see V. Gold and C. H. Rochester, *Proc. Chem. Soc.*, 403 (1960); R. L. Letsinger and O. B. Ramsay, *J. Am. Chem. Soc.*, **86**, 1448 (1964); and R. M. Johnson and C. W. Rees, *Proc. Chem. Soc.*, 213 (1964)].