

When the decomposition of 12 (0.512 g in 20 ml of cumene) was run at 80° for 4 hr, several modifications of the above procedure were used. The volatile liquids were distilled at 25° (0.5 Torr), collected in a Dry Ice-isopropyl alcohol trap, and made up to 25 ml with toluene. A 5-ml aliquot was subjected to iodometric titration. The peroxide content corresponded to a 73% yield of

tert-butyl hydroperoxide. The solid residue from the distillation was shown by ir to be phthalic anhydride, with no detectable bicumyl or acids present.

Registry No.—1, 2155-71-7; 10, 35356-77-5; 11, 35356-78-6; 12, 15042-77-0.

Ion Radicals. XXVI. Reaction of Perylene Perchlorate with Cyanide Ion¹

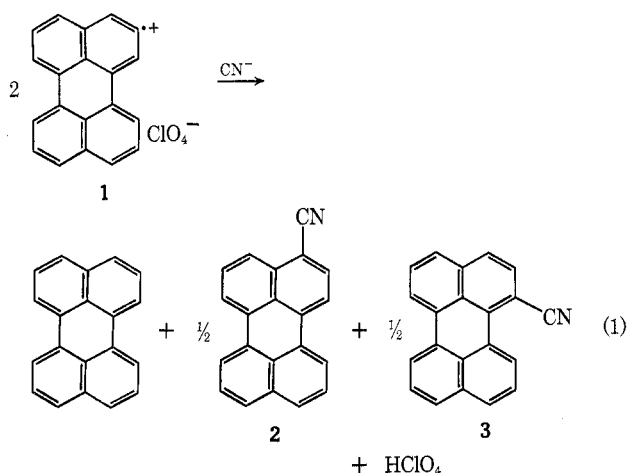
HENRY J. SHINE* AND CHARLES V. RISTAGNO²

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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Reaction of perylene perchlorate (1) with potassium cyanide in acetonitrile gave both 3- (2) and 1-cyanoperylene (3), each in 13% yield. The structure of 3 was deduced from hydrolysis to the carboxylic acid and from reaction with LiAlH₄. Whereas reduction of 2 with LiAlH₄ led to 3-formylperylene, reaction of 3 with LiAlH₄ gave perylene-1-d (4) and 1'-aza-1,12-benzoperylene-2'-d (5). The reaction of 1 with cyanide ion is the first we have encountered of substitution in the 1 as well as 3 position of 1. This is attributed to the high nucleophilicity, small size, and linearity of the cyanide ion.

In previous papers we have shown that perylene perchlorate (1) reacts with nucleophiles (NO₂⁻, OAc⁻, Bz⁻, H₂O, pyridine) in the 3 position.^{3,4} Charge densities in the perylene cation radical, according to the simple Hückel MO calculations,⁵ are in accord with this, although one would anticipate that substitution in the 1 position ($q = 0.084$) might occur as well as in the 3 position ($q = 0.110$). This has now been achieved in reaction of 1 with cyanide ion. In addition to the anticipated perylene (eq 1) and 3-cyanoperylene (2),



a third product was formed which we deduce from its analysis, parent-peak mass number (277), and reactions to be 1-cyanoperylene (3). We believe the stoichiometry^{3,4} of reaction to be as shown in eq 1, according to which the yields of 2 and 3 were each 26% of those anticipated, while the yield of perylene was greater than 100%, signifying that perylene was formed also by another reaction, *e.g.*, reduction by cyanide ion.

Compound 2 is known, having been made *via* the

sequence perylene → 3-formylperylene → 3-formylperylene oxime → 2.⁶ We confirmed the structure of our 2 by hydrolysis to perylene-3-carboxylic acid,^{6,7} by reduction with lithium aluminum hydride to 3-formylperylene,⁶ and by oxidation of the 3-formylperylene to perylene-3-carboxylic acid, as well as by the direct synthesis of authentic 2.⁶

As far as we are aware, compound 3 is new. Very few 1-substituted perylenes are known,⁸⁻¹⁰ and we have deduced the structure in the following ways.

Hydrolysis of 3 gave a carboxylic acid, mp 395°. The only known perylenecarboxylic acids are perylene-3- (mp 335°) and perylene-2-carboxylic acid (mp 342°).⁹ The acid with mp 395° had an ultraviolet spectrum similar to but not identical with the spectra of the known acids. The electronic spectra of perylene and its derivatives (alkyl,¹⁰ acyl,⁷ and carboxyl⁷) have numerous bands, and our acid, believed to be perylene-1-carboxylic acid, is no exception.

Zieger attempted to synthesize perylene-1-carboxylic acid by two routes starting with 1-bromohexahydroperylene, but was unsuccessful.⁷ We also were unsuccessful in our attempts to prepare an authentic sample of the acid by oxidation of 1-methylperylene⁸ with aqueous chromic acid, chromium trioxide in acetic acid, and potassium permanganate in acetone. We were unable to isolate products of oxidation, and it is perhaps possible that the perylene ring itself is too susceptible to oxidation to permit alkyl-group oxidation only. We were also unable to reduce 3 to 1-methylperylene by the technique of boiling with limonene over 5% palladium on charcoal.¹¹

Further evidence for the structure of 3 was obtained by reduction with lithium aluminum deuteride (LiAlD₄). Reduction of 2 with LiAlH₄ led to 3-formylperylene easily. Reduction of 3 with LiAlH₄ gave perylene and another compound, isomeric with 3, whose structure is discussed later. The course of reduction was discerned by use of LiAlD₄. This gave

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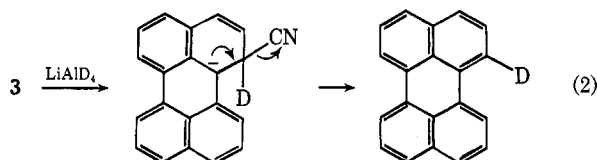
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perylene-1-*d* (**4**, 22% yield), whose identity was established by the nmr spectrum of its dianion.

The nmr spectrum of perylene-1-*d* itself was not clearly analyzable. Perylene dianion has a more clearly resolved spectrum,¹² and the effect of deuterium substitution should be more easily discernible in the dianion than in the parent hydrocarbon. This proved to be the case, as is shown in Figure 1. The splitting pattern for H-2 in the 1-*d* dianion is no longer the triplet of the 1-*h* dianion. Instead, a five-line pattern is observed, consisting of a triplet for H-2 ($J = 8$ Hz) and a doublet for H-2' ($J = 7$ Hz). The multiplet for the H-1, H-2 protons is distorted in the spectrum of the 1-*d* dianion, and integration of the spectrum gave, as anticipated, a ratio H(1,3,3'):H(2,2') of 7:4. Integration of the undeuterated dianion spectrum gave the expected ratio 8:4. It is evident that attempted reduction of **3** ended in replacement of cyanide by deuteride ion (eq 2).



The second product (54% yield) from attempted reduction of **3** is believed to be a new compound, 1'-aza-1,12-benzoperylene-2'-*d* (**5**). This compound is like its carbocycle analog 1,12-benzoperylene (**6**).¹³ Both compounds crystallize in yellow-green plates, and have similar ultraviolet spectra (Table I).

TABLE I

ULTRAVIOLET SPECTRA OF 1,12-BENZOPERYLENE (**6**)^a AND 1'-AZA-1,12-BENZOPERYLENE-2'-*d* (**5**) IN ETHANOL

Compd	Spectrum, nm (log ϵ) ^b
5 ^c	413 (3.93), 389 (3.87), 376 (4.02), 370 (4.03), 358 (3.96), 330 (3.61), 315 (3.55), 298 (4.40)
6 ^b	407 (2.70), 388 (4.50), 367 (4.40), 348 (4.00), 331 (3.82), 303 (4.76), 292 (4.65)

^a Reference 13. ^b Wavelengths have been rounded off to whole numbers. ^c We thank Mr. J. D. Cheng for recording the ultraviolet spectrum.

Further evidence in support of structure **5** was obtained from the change in ultraviolet spectrum on acidifying the solution (see Experimental Section). A shift to longer wavelengths occurred, which was reversed by neutralizing the acid. This behavior is characteristic of aza hydrocarbons of this type, e.g., 9-azaphenanthrene.¹⁴ In the case of **5** addition of acid also causes an increase in fine structure, and the spectrum had characteristics similar to those of a substituted perylene.

The parent-peak mass number of **5** was 278, as required by the proposed structure.

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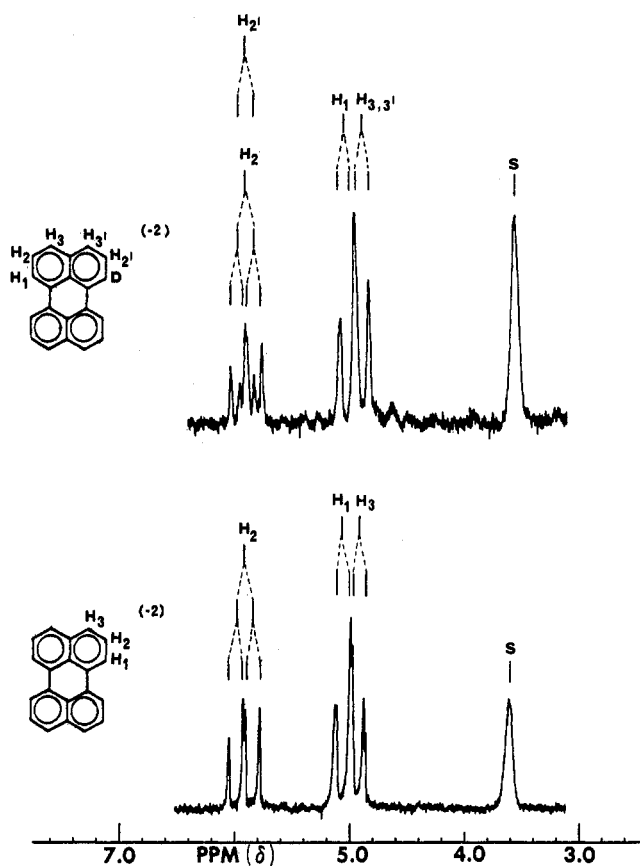
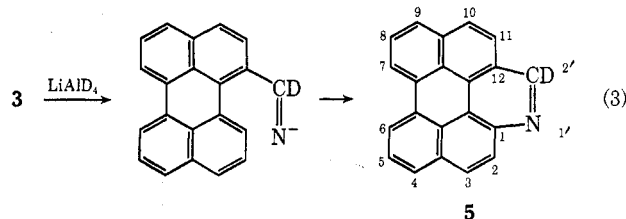
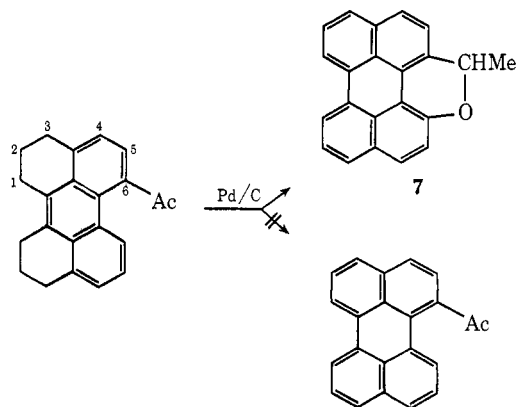


Figure 1.—60-MHz spectra of perylene dianion and perylene-1-*d* dianion in THF-*d*₈. The counterion is sodium. The peak (s) at 3.6 ppm arises from THF-*d*₇.

It appears that reaction of **3** with hydride (deuteride) ion results in cyclization (eq 3) as well as cyanide-ion



displacement. A similar reaction has been proposed for the attempted dehydrogenation of 6-acetylhexahydroperylene, which led instead to the cyclic ether **7**.⁹



In contrast, 5-acetylhexahydroperylene underwent the desired dehydrogenation. The situation is similar to our results with reduction of **2** and attempted reduction

of 3. That is, the groups in the 1 position of perylene seem not to behave like those in the 2 and 3 positions. We have not been able to find information in the literature on hydride reductions of compounds analogous to 3, e.g., 4-cyanophenanthrene, and we have begun to study such compounds ourselves.

The reaction of 1 with cyanide ion constitutes, as far as we know, the most straightforward preparation of monocyanoperylene. Anodic cyanation is a fairly well-known technique¹⁵ but also, as far as we know, has not been applied to perylene.

The literature contains references to the formation of dicyanoperylene by reaction of dihalogenoperylene with cyanide ion.¹⁶ Attempts to make a monocyanoperylene were unsuccessful until the work of Buu-Hoi with 2.⁶

The formation of 1-cyanoperylene from reaction of 1 with cyanide ion may be attributable to the linearity, small size, and high nucleophilicity of the cyanide ion. We have attempted a similar reaction with azide ion, but the reaction is much more complex than the cyanide-ion reaction and is still being pursued.

Experimental Section

Perylene perchlorate (1) was prepared electrochemically. Our earlier technique⁴ was altered to give a mixture of 1 and perylene which contained 94% instead of 60-70% of 1. In place of the H cell, a copper cathode was placed in a Soxhlet thimble which contained electrolyte solution. The thimble was suspended within the cylindrical platinum gauze anode (Sargent-Welch, S-29672, diameter 40 mm, height 35 mm) held in a solution of electrolyte and perylene. Portions of perylene were added to the anode solution periodically during electrolysis, which proceeded for 1-2 hr at 1.2 V. The content of 1 in the solid which deposited on the anode was determined by iodimetry.⁵

Reaction of 1 with KCN.—A suspension of 65 mg (1.0 mmol) of KCN (previously crystallized from methanol and dried under vacuum) in 50 ml of acetonitrile (MeCN) was stirred under nitrogen in an erlenmeyer flask. To this was added 105 mg (0.28 effective mmol) of 1. The resulting purple mixture was stirred for 15 min, after which time it became yellow-brown, had a strong green fluorescence, and gave a negative starch-iodide test for cation radical. Unreacted KCN was filtered off and washed well with warm benzene. Tlc on both silica gel and alumina gave three spots. Column chromatography [4 × 50 cm, silica gel 70-325 mesh ASTM, E. Merck, 2:1 petroleum ether (bp 30-60°):benzene] gave two fractions. The first was perylene, 48 mg (0.19 mmol, 68%). The second consisted of 22 mg of orange solid, mp 160-167°, which gave two spots on tlc, and whose ir (KBr) had bands at 2212 and 2225 cm⁻¹. Column chromatography of the orange solid (4 × 50 cm, neutral alumina, Woelm, 2:1 petroleum ether:benzene) gave two 10-mg (0.036 mmol, 13%) fractions. Each was crystallized from ethanol. The first eluted compound was shown (see later) to be 1-cyanoperylene (3), mp 236-237°.

Anal. Calcd for C₂₁H₁₁N: C, 91.0; H, 3.97; N, 5.05. Found: C, 91.0; H, 4.19; N, 5.31.

Compound 3 had λ_{max} (methanol) at 452, 429, 288, and 261 nm, and ir -C≡N at 2212 cm⁻¹. The mass spectrum showed a parent-peak mass number of 277.

The second eluted compound was shown (see below) to be 3-cyanoperylene (2), mp 231-232° (lit.⁶ mp 228°).

Anal. Calcd for C₂₁H₁₁N: C, 91.0; H, 3.97; N, 5.05. Found: C, 91.2; H, 4.25; N, 5.21.

Compound 2 had λ_{max} (methanol) at 452, 429, 256, and 249 (sh) nm, and ir -C≡N at 2225 cm⁻¹.

Synthesis of Authentic 3-Cyanoperylene.—A sample of 3-formylperylene, mp 233-234° (lit.⁶ mp 236°), was prepared. This was converted into the oxime, mp 255°, and the oxime was dehydrated as described,⁶ giving 3-cyanoperylene, mp 230-231° (ethanol), undepressed by mixture with 2.

Hydrolysis of 2 to Perylene-3-carboxylic Acid.—A solution of 20 mg (0.072 mmol) of 2 in 5 ml of ethanol and 5 ml of dioxane was boiled over solid NaOH for 72 hr. The solution was decanted, the solvent was removed under vacuum, and the yellow solid was washed with water and benzene. The solid was then stirred with 50 ml of 10% hydrochloric acid for 2 hr and collected, giving 20 mg (0.068 mmol, 94%) of orange solid. Crystallization from acetic acid gave perylene-3-carboxylic acid: mp 333° dec; λ_{max} (methanol) 441, 416, 393 (sh), and 247 (sh) nm; ir bands at 3200-2300 (br) and 1680 cm⁻¹.

Synthesis of Authentic Perylene-3-carboxylic Acid.—A solution of 12.5 mg (0.045 mmol) of 3-formylperylene in 10 ml of acetone was stirred at 50° with an excess of aqueous KMnO₄ solution for 3 hr. Precipitated MnO₂ was filtered and the solvent was removed under vacuum. Extraction of the residue with hot benzene gave 4 mg (0.014 mmol, 33%) of perylene-3-carboxylic acid, mp 332° dec (lit.⁶ mp 334° from hydrolysis of 3-cyanoperylene).

Reduction of 2 with LiAlH₄ to 3-Formylperylene.—To a solution of 10 mg (0.036 mmol) of 2 in 25 ml of dry THF at 0° was added several milligrams of LiAlH₄. The mixture was stirred under nitrogen for 1 hr at 0°, poured onto ice-cold 10% hydrochloric acid, and extracted with benzene, giving 8 mg (0.028 mmol, 79%) of 3-formylperylene, mp 232-234°.

Hydrolysis of 3 to Perylene-1-carboxylic Acid.—The method was as described for the hydrolysis of 2, and gave 16 mg (0.054 mmol, 75%) of what we believe to be perylene-1-carboxylic acid: mp 395° (1:1 benzene:acetic acid); λ_{max} (methanol) 441, 417, 395, 371, 356, 284, and 274 nm; ir bands at 3200-2300 (br) and 1660 cm⁻¹.

Anal. Calcd for C₂₁H₁₂O₂: C, 85.1; H, 4.05. Found: C, 85.0; H, 4.15.

These characteristics do not correspond with those reported for perylene-3^{6,7} and perylene-2-carboxylic acid.⁷

Reaction of 3 with LiAlD₄.—Several attempts to reduce 3 with LiAlH₄ to 1-formylperylene failed and gave, in part, perylene instead. In order to diagnose the course of this reaction, LiAlD₄ (99% d, Merck Sharp, and Dohme) was used. To a cold (-5°) solution of 60 mg (0.22 mmol) of 3 in 30 ml of dry THF was added a cold solution of 20 mg (0.77 effective mmol) of LiAlD₄. The solution was stirred for 4 hr, decomposed by adding 5 ml of 15% aqueous NaOH, diluted with saturated aqueous NaCl, and extracted with benzene. The benzene extract was chromatographed on neutral alumina (Woelm). Elution with benzene gave 12 mg (0.05 mmol, 22%) of perylene-1-d (4). Elution with 10:1 benzene:ether gave 32 mg (0.12 mmol, 54%) of yellow-green solid, mp 307-308°, which we believe to have the structure 5.

Anal. Calcd for C₂₁H₁₀DN: C, 90.6; H, 4.34; N, 5.03. Found: C, 90.7, 90.9; H, 3.84, 4.08; N, 4.93.

The mass spectrum showed a parent-peak mass number of 278.

Addition of acid to the solid or its solution gave λ_{max} 445, 420, 377, 358, 300, 277, and 250 nm. This shift to longer wavelengths was reversed by adding base to the acidic solution.

Conversion of 4 to Perylene-1-d Dianion.—4 (12 mg) was placed in an nmr tube. A small piece of sodium was held in the top of the tube by a constriction, and the tube was sealed into a glass assembly attached to a reservoir containing dry THF-d₈. After the assembly was evacuated, ca. 0.5 ml of THF-d₈ was distilled into the nmr tube. Reduction of 4 was accomplished by bringing the solution in contact with the sodium over a period of several hours. The nmr spectrum was recorded on a Varian A-60A spectrometer and is given in Figure 1.

Registry No.—1, 12576-63-5; 2, 35426-74-5; 3, 35426-75-6; 5, 35426-76-7; 6, 191-24-2; perylene-3-carboxylic acid, 7350-88-1; 3-formylperylene, 35438-63-2; perylene-1-carboxylic acid, 35426-79-0; cyanide ion, 57-12-5.

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