A NEW AZACYANOCARBON, C4N4: TRICYANOMETHANIMINE

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Abstract - 2,2-Dichloroethylene-1,1-dicarbonitrile reacted with sodium azide to give 2,2diazidoethylene-1,1-dicarbonitrile, which underwent thermolysis to give tricyanomethanimine, C_4N_4 . The latter is as reactive as TCNE toward electron-rich molecules.

Although the rich chemistry of the highly electrophilic molecules tetracyanoethylene² (1) and carbonyl cyanide³ (2) has been extensively documented, no report dealing with tricyanomethanimine (3) has appeared in the literature. We now offer a preliminary report on the synthesis and chemistry of this new azacyanocarbon, $C_{4}N_{4}$.



Reaction of a solution of 2,2-dichloroethylene-1,1-dicarbonitrile⁴ (4) (200 mg, 1.34 mmole) in acetone (1 mL) with an excess of sodium azide (400 mg, 6.00 mmole) in acetone-water (4 mL, 1:1) at -20 to -15°C afforded the 2,2-diazidoethylene-1,1-dicarbonitrile (5) as an orange liquid: IR (neat): 2160 (C-N₃), 2240 (C=N) cm⁻¹.



This was dissolved in dry benzene (10 mL) and then added to hot (60 - 65°C) benzene or 1,2dichloroethane (60 mL) and stirred under argon for 1 hr.⁵ The IR spectrum of this solution shows the characteristic C-N (1714 cm⁻¹) and C=N (2323, 2246, and 2240 cm⁻¹) bands. No azide absorption at 2160 cm⁻¹ was present. ¹³C-NMR of a dilute solution of C4N4 in d6benzene showed three CN peaks at 107.5, 109.3, and 110.15 ppm.



Evaporation of the solvent *in vacuo* resulted in the rapid formation of a light yellow solid, whose IR spectrum does not show the C-N stretching. Our efforts towards the isolation of (3) were frustrated by its rapid polymerization. However, a solution of (3) in benzene or dichloroethane remains unchanged for two days at 5 - 10°C as evidenced by its IR spectrum.

To further prove the presence of (3) in solution, we made the following cycloadducts: Reaction of (3) with 2,3-dimethyl-1,3-butadiene resulted in the formation of (6)⁶ (48% yield, based on starting compound (4)).



M.p. 80 - 80.5°C; IR(KBr): 2227 cm⁻¹ (C=N); ¹H-NMR (CDCl₃, 250 MHz); δ 1.7, 1.8 (s, 6H, 2CH₃), 2.95 (s, 2H, CH₂), 3.95 (s, 2H, N-CH₂); ¹³C-NMR (CDCl₃): 15, 18 (C₈, C₇), 38 (C₅), 50 (C₂), 49 (C₆), 110, 111 (C₉, C₁₀, C₁₁), 120, 122 (C₃, C₄); MS: m/e 186 (M⁺).

Reaction of (3) with cyclopentadiene similarly afforded adduct (7),



which has previously been synthesized and characterized in our laboratories by the following method:⁷



¹H-NMR (CDCl₃): § 2.1 (2H, CH₂), 4.2 (1H, (NC)₂C-CH), 4.9 (1H, N-CH), 6.7 and 6.9 (2H, HC-CH).

Deeply colored charge transfer complexes were obtained with moderately electron-rich compounds such as anisole or hexamethylbenzene. The more electron-rich N,N-dimethylaniline underwent electrophilic aromatic substitution to give (8).⁶



IR (KBr): 2173 (C=N), 1612 (C-N) cm⁻¹. ¹H-NMR (CDCl₃): δ 3.2 (6H, 2CH₃), 6.8 and 8 (ring). The structure **(8)** was proven by hydrolysis to ethyl 4-dimethylaminobenzoate **(10)**.



This reaction offers analogy to the tricyanovinylation reaction of tetracyanoethylene with N,N-dimethylaniline.⁸ Structures (9) and (10) were proven by IR and NMR.

p-Methoxystyrene reacted spontaneously with (3) to give a 1:1 alternating copolymer.⁶ IR (KBr): 2210 and 2100 cm⁻¹ (C=N). ¹H-NMR (CDCl₃): δ 6.5 - 7.5 (broad), and 3.8 (broad).

Cyclic voltammetry of $a \approx 5 \times 10^{-4}$ M benzene solution of (3) showed an irreversible reduction peak at -0.16V in 0.1M tetrabutylammonium tetrafluoroborate in dichloromethane using Ag/0.1M AgNO₃ in acetonitrile as a reference electrode and a scan rate of 100mV/sec. For comparison under the same conditions, TCNE showed a reversible peak at -0.11V.

M1 Molecular orbital calculations⁹ found that the lowest unoccupied molecular orbital (LUMO) level for (3) (-2.20eV) lies at higher energy than the LUMO for (1) (-2.52eV) which is consistent with the electrochemical results. On the other hand, the highest occupied molecular orbital (HOMO) for (3) lies -0.8eV lower in energy than the HOMO of (1). The heat of formation of (3) is 135.3 kcal/mole, and it is thermodynamically more stable than the TCNE by 17 kcal/mole.

We are continuing to investigate the chemistry of tricyanomethanimine (3) and related electron-poor imines.

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