

Unsaturated Hydrogen-Free Halogeno Cyano Compounds

I. Synthesis and Properties of Iodocyanoacetylene ¹

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Iodocyanoacetylene, m.p. 152°C, has been prepared by iodination of cyanoacetylene. Chemical and physical characteristics of the compound are described. The electric dipole moment was found to be 4.59 ± 0.05 Debye at 25.0°C.

For the study of charge transfer bonds in solids, molecules exhibiting electron donor as well as electron acceptor properties are of considerable interest. The simplest carbon compound containing both donor and acceptor atoms would be a cyanogen halide. Crystals of cyanogen bromide and cyanogen iodide have been shown ^{2,3} to consist of molecules in linear arrangements

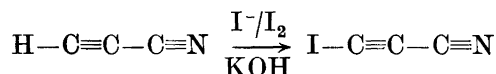


in which, according to Hassel,⁴ the intermolecular nitrogen halogen bonds may be of the charge transfer type.

A similar linear arrangement of the molecules would be expected (Hassel) to exist in an acetylenic homologue of the cyanogen halide, such as iodocyanoacetylene, $\text{I}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$. The present paper gives the synthesis and general properties of this compound.

The iodocyanoacetylene was prepared by iodination of cyanoacetylene,⁵ by analogy with the preparation of di-iodoacetylene ⁶ and di-iododiacetylene ⁷ from the respective acetylenes.

The cyanoacetylene was treated with a potassium iodide/iodine solution under alkaline conditions to give the iodocyanoacetylene (iodopropiolonitrile)



Although cyanoacetylene has been reported to be vigorously attacked by aqueous potassium hydroxide, forming tar-like products,⁵ the competing reaction of the cyanoacetylene with the hypoiodite reagent was fast enough to produce considerable amounts of the iodo-substituted compound. From the reaction mixture the precipitated iodocyanoacetylene could be isolated

as a fine powder, which gave a snow-white crystalline product upon recrystallisation and sublimation under reduced pressure. It had a characteristic iodoform-like odour, and a pure sample melted sharply at 152–152.5°C (s.c.) without decomposition.

An alternative approach to the halogenation of cyanoacetylene was undertaken in attempts to synthesize bromocyanoacetylene, as described in a following paper.⁸ Preparation of iodocyanoacetylene according to this procedure gave a rather pure reaction product in excellent yield (about 60 %).

Iodocyanoacetylene appears in different modifications. By sublimation at moderately low temperatures it deposits as very thin needles, which could be more than 20 mm long. When kept at a higher temperature (around 0°C) they broke down to a fine powder, without observable change of melting point.

Iodocyanoacetylene is moderately stable to air and light. On exposure to air it is converted to an insoluble reddish-brown product in the course of a few days. In a light-protected, evacuated tube in the cold it can be kept for a longer time.

Spectroscopic investigations of the compound have been undertaken in the infrared, ultraviolet and micro-wave⁹ regions.

Infrared absorption spectra were recorded from 4000–270 cm⁻¹. With rock salt optics the following bands were observed: 2277, 2138 cm⁻¹ (carbon tetrachloride solution), 2275, 1027 cm⁻¹ (carbon disulphide; the band at 2138 cm⁻¹ is obscured because of strong solvent absorption). In the cesium bromide region three bands appeared at 488, 396, and 296 cm⁻¹, respectively (carbon disulphide). The three bands at 2277 (2275), 2138, and 1027 cm⁻¹ can probably be assigned to the C≡N, C≡C and C–C stretching modes, respectively. The distinct bands at 488 cm⁻¹ can possibly be related to the I–C≡ stretching frequency, the observation of which has hitherto not been reported in the literature.

In the ultraviolet region three maxima of slightly increasing intensity were located at approximately 273 (log ϵ 2.55), 256 (log ϵ 2.67) and 243 m μ (log ϵ 2.73). Additionally, a shortest wave-length and strongest absorption band showed a double maximum at 230 (log ϵ 3.09) and 226 m μ (log ϵ 3.08).

As a considerable degree of polarity would be expected for the iodocyanoacetylene molecule, the electric dipole moment of the compound has been measured. The relatively high value of $\mu = 4.59$ Debye was found, which is interesting when compared with the reported value of the dipole moment of cyanogen iodide $\mu = 3.71$ Debye.¹⁰

X-Ray investigations of the room temperature modification carried out by Hassel, R  mning and Borgen,¹¹ confirm the linearity of the molecules, which are mutually arranged in straight chains, as expected for this type of compound.

EXPERIMENTAL

Preparation of iodocyanoacetylene. The cyanoacetylene used for the synthesis was prepared according to Moureu and Bongrand⁶ by a synthesis in four steps from acetylenedicarboxylic acid monopotassium salt \rightarrow propiolic acid \rightarrow methyl propiolate \rightarrow propiolic acid amide \rightarrow propiolonitrile (cyanoacetylene).

From a reservoir of cyanoacetylene a portion of about 100 mg was distilled in an atmosphere of nitrogen under 25 mm Hg pressure into a reaction flask cooled in dry

ice. After changing to an ice-water bath nitrogen was let in to raise the pressure to atmospheric level, and half-normal potassium hydroxide (25 ml) was added under stirring. Successively a cold solution of iodine (12.8 g) and potassium iodide (14.0 g) in water (10 ml) was added dropwise. The colour immediately vanished and a fine, crystalline, heavy precipitate appeared. The addition was continued until the decolouration ceased.

The reaction mixture was extracted with ether and excess of iodine removed by shaking with a saturated solution of sodium thiosulphate. After drying over anhydrous sodium sulphate and removal of the solvent in vacuum a powdered, yellowish residuum was isolated. Recrystallisation from chloroform and repeated sublimation at 1 mm Hg pressure from room temperature to dry ice temperature gave a snow-white, compact sublimate, adhering strongly to the glass wall. When the end of the sublimation tube was placed in a Dewar vessel at a moderate distance from a layer of dry ice, iodoacyanoacetylene deposited as very thin needles of varying length. A pure sample melted at 152–152.5°C (s.c.) without discolouration.

Preparation of the compound on a larger scale yielded a rather impure reaction product. From 0.7 g of cyanoacetylene 1.25 g of crude material could be isolated. Recrystallisation of the non-sublimable product gave 200 mg (8 %) of well crystallising material, which could be purified further by sublimation.

Improved procedure for preparation of iodoacyanoacetylene. To an ice-cooled solution of cyanoacetylene (0.150 g) in water (7 ml) was added a cold solution of potassium iodide (0.94 g) and iodine (0.84 g) in water (1 ml). By dropwise addition of half-normal potassium hydroxide a fine crystalline precipitate appeared spontaneously. Addition was continued until precipitation seemed to be complete (about 7 ml KOH). Filtration and washing on the filter with a few drops of ethanol gave a snow-white, fine crystalline product (0.400 g) m.p. 140°C (s.c., decomp.) Yield about 60 %.

The infrared spectra were recorded on a Perkin-Elmer Infrared Spectrometer Model 21 (NaCl and CsBr prisms) in carbon tetrachloride and carbon disulphide solutions.

The ultraviolet spectra were recorded on a Beckman DK-1 Recording Spectrometer, using cyclohexane as a solvent.

Dipole moment measurements. For determination of the electric dipole moment an apparatus available in this institute was used. A dipole moment of 4.59 ± 0.05 Debye in benzene solution at 25.0°C was found.

The melting points (uncorrected) in sealed capillaries (abbreviated s.c.) were measured on a Hoover Capillary Melting Point Apparatus.

Acknowledgements. The author expresses her thanks to Mag.sc. Else Augdahl, University of Oslo, and Cand.real. G. Eia, Central Institute for Industrial Research, Oslo, for measurements and discussion of the infrared spectra. Thanks are due to Cand.real. T. Bjorvatten for determination of the electric dipole moment.

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Received April 9, 1963.