TABLE I

ω-BROMOALKYL QUATERNARY AMMONIUM SALTS: Br—$(CH_2)_n$—N⊕R′R_2Br⊖

	n	NR_2	R′	M.p., °C.	Formula	Ionic bromine, % Calcd.	Ionic bromine, % Found
I	2	$N(CH_3)_2$	CH_3	229[b]	$C_5H_{13}Br_2N$	32.35	32.47
II	2	Pyrrolidino	CH_3	223	$C_7H_{15}Br_2N$	29.27	29.42
III	3	$N(CH_3)_2$	CH_3	205[c]	$C_6H_{15}Br_2N$	30.61	30.93
IV	3	$N(CH_3)_2$	$C_6H_5CH_2$	156–158	$C_{12}H_{19}Br_2N$	23.70	24.09
V	3	$N(C_2H_5)_2$	CH_3	120–130	$C_8H_{19}Br_2N$	27.64	27.71
VI	3	$N(C_2H_5)_2$	C_2H_5	146–148[d]	$C_9H_{21}Br_2N$	26.33	26.55
VII	3	Pyrrolidino	CH_3	177–179	$C_8H_{17}Br_2N$	27.84	27.96
VIII	3	Piperidino	CH_3	190–193	$C_9H_{19}Br_2N$	26.54	26.60
IX	3	Morpholino	CH_3	143–145	$C_8H_{17}Br_2NO$	26.37	26.58
X	3	C_5H_5N[a]		128–129[e]			
XI	4	Pyrrolidino	CH_3	96[f]			
XII	5	$N(CH_3)_2$	CH_3	133–136	$C_8H_{19}Br_2N$	27.64	28.10
XIII	6	$N(CH_3)_2$	CH_3	106–108	$C_9H_{21}Br_2N$	26.36	26.49
XIV	10	$N(CH_3)_2$	CH_3	122–128	$C_{13}H_{29}Br_2N$	22.25	22.28

[a] Pyridine derivative. [b] M. Krüger and P. Bergell, *Ber.*, **36**, 2901 (1903), reported m.p. 230–231°. [c] R. Lucius, *Arch. Pharm.*, **245**, 249 (1907), reported m.p. 208°. [d] R. Lucius, *ibid.*, p. 254, gave m.p. 227–228° for this compound. [e] M.p. of the crude material (ionic halogen determination indicated it to contain 9% of the bis salt). [f] M.p. of the crude material containing *ca.* 6% of the bis salt.

of 48% hydrobromic acid and 4 ml. of ethanol was refluxed for 15 hours. The solution was concentrated *in vacuo* to an oily residue. The oil was dissolved in alcohol, precipitated with ether and then taken to dryness several times under reduced pressure with the addition of benzene. There was obtained 10.5 g. of hygroscopic product, m.p. 190–193°, representing a 70% yield in the final step.

Acknowledgment.—Ionic halogen determinations were performed by Mr. Donald L. Miller.

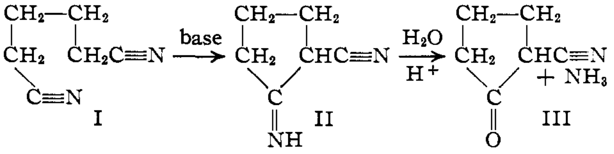
RESEARCH LABORATORIES
IRWIN, NEISLER & CO.
DECATUR, ILLINOIS

Structure of the Cyclic Condensation Product of Adiponitrile

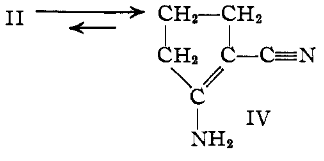
BY C. F. HAMMER AND R. A. HINES

RECEIVED FEBRUARY 26, 1955

The base-catalyzed cyclization of adiponitrile (I) is a well-known reaction.[1,2] Previously, the cyclic reaction product has been assigned the structure of 2-cyanocyclopentylidene imine (II),[2] largely because it is hydrolyzed very readily to 2-cyanocyclopentanone (III), as indicated by the equation

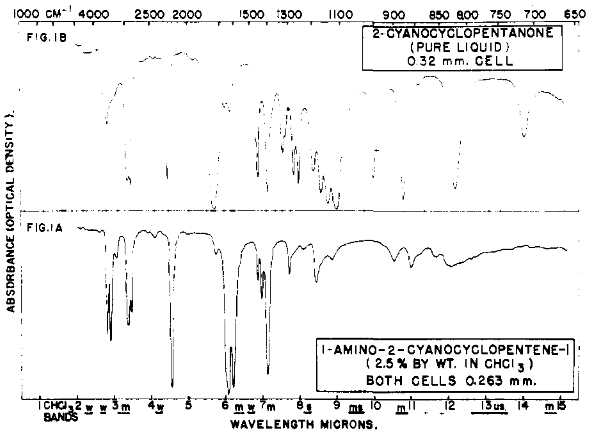


However, we propose that the cyclic product obtained from I exists principally as the enamine of II, 1-amino-2-cyanocyclopentene-1 (IV)



The evidence for this enamine structure is found in the infrared and ultraviolet spectra of the cyclic product. An analogous situation for conjugated aminoesters exists with respect to ethyl aminocrotonate.[3,4]

The infrared spectrum of the product obtained by cyclization of I is shown in Fig. 1-A. The absorption at 2189 cm.$^{-1}$ indicates a rather unusual conjugated nitrile; the presence of an $-NH_2$ group is indicated by absorptions at 3512, 3420 and 1645 cm.$^{-1}$; and an olefinic linkage characteristic of cyclopentene is indicated by absorption at 1605 cm.$^{-1}$. Since it has been shown by Kitson and Griffith[5] that unconjugated nitriles absorb at 2250 cm.$^{-1}$ and that normal conjugated nitriles absorb at 2225 cm.$^{-1}$, it may be presumed that the further shift of the nitrile absorption to 2189 cm.$^{-1}$ is due to the influence of the amine group. The location of the absorption peak at 2189 cm.$^{-1}$ was determined more accurately by scanning this region at higher resolution with the use of a calcium fluoride prism.



The infrared spectrum of the hydrolysis product III is shown in Fig. 1-B. In contrast to the spectrum of Fig. 1-A, this shows absorption of a normal unconjugated nitrile at 2250 cm.$^{-1}$ and of a ketone at 1755 cm.$^{-1}$; there is no olefinic absorption at 1605 cm.$^{-1}$. Therefore, it is evident that in this

---

(1) S. R. Best and J. F. Thorpe, *J. Chem. Soc.*, **95**, 685 (1909).

(2) J. F. Thorpe, *ibid.*, **95**, 1901 (1909).

(3) K. von Auwers and W. Susemihl, *Ber.*, **63**, 1072 (1930).

(4) S. A. Glickman and A. C. Cope, THIS JOURNAL, **67**, 1017 (1945).

(5) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

case the tautomeric equilibrium favors strongly the ketone structure III.

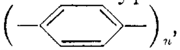
The ultraviolet spectrum of the cyclic product obtained from adiponitrile offers further evidence for the existence of an unusual, conjugated nitrile group since there is a major absorption peak at 263 mμ. Simple aliphatic nitriles do not absorb appreciably in this region, but conjugated nitriles and conjugated aminoesters (*e.g.*, ethyl β-aminocrotonate) do absorb strongly at about 265 mμ.[4] The absorptivity (ε) is 13,000 liters per mole-centimeter which is about 130 times as large as observed for normal conjugated nitriles; thus the amine group has a powerful effect on the ultraviolet absorption of this conjugated nitrile group. This is in concordance with the observations made on ethyl β-aminocrotonate by Glickman and Cope,[4] on β-aminocrotonitrile by von Auwers and Susemihl,[3] and with the unusually low infrared nitrile frequency we have observed for IV.

POLYCHEMICALS DEPARTMENT
E. I. DU PONT DE NEMOURS & CO., INC.
DU PONT EXPERIMENTAL STATION
WILMINGTON, DELAWARE

Synthesis and Properties of Fluorinated Polyphenyls[1,2]

BY M. HELLMANN, A. J. BILBO AND W. J. PUMMER

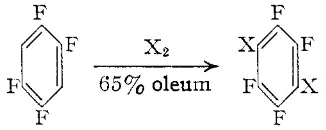
RECEIVED FEBRUARY 21, 1955

Polyphenyl of the general structure , which has been prepared by the Wurtz reaction[3] on *p*-dichlorobenzene, is a high-melting, sparingly soluble powder. Although this polymer exhibits high thermal stability, it loses hydrogen at temperatures above 500°. Since the C–F bond is stronger than the C–H bond, replacement of the hydrogen by fluorine in the polyphenyl should enhance the thermal stability of the molecule. Furthermore, such a substitution also would make the molecule highly resistant to oxidation.

In order to obtain the desired fluorinated polymers, 1,2,4,5-tetrafluorobenzene[4] was chosen as the starting material. This compound was brominated and iodinated in 65% oleum. The bromination was described recently.[5] Iodination proceeded under the same conditions and gave the diiodo compound in good yield. Chlorination, using sulfuryl chloride and 65% oleum, was unsuccessful; tetrafluorobenzene was recovered unchanged. These reactions are summarized in Table I.

TABLE 1

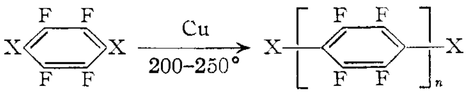
HALOGENATION OF 1,2,4,5-TETRAFLUOROBENZENE



X	Yield, %	M.p., °C.
I	81	109–111
Br	78	76–77
Cl (used SO_2Cl_2)	no reacn.	

Condensations of 1,4-dibromo- and 1,4-diiodobenzene with metals and organometallic reagents failed to give a polymer, with the exception of a modified Ullmann reaction in which activated copper powder was mixed with the dihalo compound and heated at 200–250°. The reaction with sodium in ether and dioxane led to degradation, probably because the metal attacked fluorine as well as bromine and iodine. A method described recently by Henne[6] for the coupling of perfluoroalkyl bromides using Zn and acetic anhydride also was tried without success. Grignard reagents and organolithium compounds reacted with dibromo- and diiodotetrafluorobenzene giving rise to a mixture of products which were difficult to separate and identify.

By the Ullmann reaction according to the following scheme



low polymers were obtained. These polymers could be separated into two fractions. One, soluble in benzene, showed an average degree of polymerization of 4–5 (mol. wt. 750–1000). The other, an insoluble fraction, had an average degree of polymerization of 8–10 (mol. wt. 1300–1700). The molecular weight was determined by chemical analysis for bromine or iodine, assuming two halogen atoms per polymer chain. Additional confirmation of the structure of these polymers was obtained by mass spectrometer measurements. These were performed by evaporating the polymer directly into a mass spectrometer and identifying the mass peaks.[7] By raising the temperature stepwise from 189 to 431°, peaks corresponding to ions from $(C_6F_4)_3X_2$ to $(C_6F_4)_{11}X$ were identified. The amount of degradation within this range of temperature appeared to be very small as no appreciable amounts of fluorocarbon fragments were detected. This observation indicates high thermal stability as well as resistance to mild electron bombardment. The insoluble fraction of the polymer from diiodotetrafluorobenzene also was subjected to heating in an evacuated tube at 500° for 1 hour. The material darkened and the presence of iodine was noticeable but the bulk of the material remained intact.

Experimental

1,4-Diiodo-2,3,5,6-tetrafluorobenzene.—Iodine (13 g.) and 65% fuming sulfuric acid (15 ml.) were mixed and stirred at room temperature for 30 minutes. Then 5 g. of tetrafluorobenzene[4] was added gradually over a period of 10 minutes. Subsequently, the mixture was heated on a water-bath at 55–60° for 3 hours. The mixture was cooled and poured over crushed ice. A dark solid formed which was filtered, washed with aqueous sodium bisulfite and dried. This material was recrystallized from a methanol-water mixture, giving 11 g. of a white solid melting at 109–111°; yield 81%.

---

(1) This paper is based on work sponsored by the Ordnance Corps, United States Department of the Army.

(2) Presented as part of the Symposium on Fluorine Chemistry, Division of Industrial & Engineering Chemistry, at the 126th Meeting of the American Chemical Society in New York City, September, 1954.

(3) G. Goldfinger, *J. Polymer Sci.*, **4**, 93 (1949).

(4) G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort and R. R. Blough, THIS JOURNAL, **73**, 145 (1951).

(5) M. Hellmann and A. J. Bilbo, *ibid.*, **75**, 4590 (1953).

(6) A. L. Henne, *ibid.*, **75**, 5750 (1953).

(7) P. Bradt and F. L. Mohler, National Bureau of Standards Report No. 3345, June 11, 1954 (accepted for publication in *Anal. Chem.*).