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Heptafulvenes. VI. The Structure of 2, 3-Diamino-8, 8-dicyanoheptafulvene Hydrochloride

By Tadahiro KATO*

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-cho, Sendai

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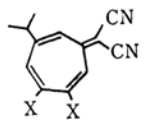
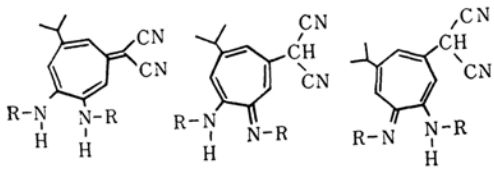
2, 3-Diamino- and 2, 3-bismethylamino-8, 8-dicyanoheptafulvenes gave the corresponding crystalline salts of hydrochloride. From the infrared and ultraviolet spectra, it was concluded that these hydrochlorides are the derivatives of the hydrochloride of 2-aminotropoimine.

In a previous paper,[1] it has been reported that 5 - isopropyl - 2, 3 - dimethoxy - 8, 8 - dicyanoheptafulvene (I) yielded the corresponding diamino compounds II, III and IV respectively, by the reactions with the amines RR'NH (R, R'=H and/or CH_3). It is possible that, besides the heptafulvene structure (A), II and III take a tautomeric 2-aminotropoimine structure, such as B or C.



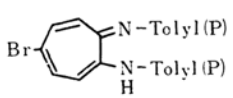
(I) X=OCH_3 (II) X=NH_2
(III) X=$NHCH_3$ (IV) X=$N(CH_3)_2$



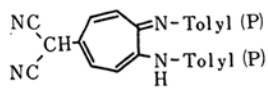
(A) (B) (C)

R=H, CH_3

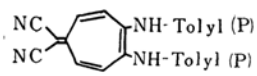
Recently Brasen and his coworkers[2,3] have reported that the product obtained by the reaction of 4-bromo-1-(*p*-tolylamino)-7-(*p*-tolylimino)-1, 3, 5-cycloheptatriene (V) with malononitrile is not 2-aminotropoimine (VIa), but 3, 4-bis-(*p*-tolylamino)-8, 8-dicyanoheptafulvene (VIb).



V



VIa



VIb

The infrared absorption spectra of II, III and IV display absorptions at 2200—2190 cm^{-1} due to the presence of conjugated cyano groups; and four strong absorption bands of two primary amino groups in II, while two strong bands assigned to two secondary amino groups in III are observed in the 3500—3100 cm^{-1} region (Table I).

TABLE I. INFRARED SPECTRA OF 2,3-DIAMINO-8,8-DICYANOHEPTAFULVENES AND THEIR HYDROCHLORIDES

Compound	IR spectra, cm^{-1}		
	NH region	CN region	
II	3490, 3420, 3310, 3254	2170 (S) 2195 (S)	1693, 1643, 1610
III	3380, 3200	2170 (S) 2195 (S)	1625
IV	—	2175 (S) 2195 (S)	1605
VII	3140 3300	2270 (W)	1690, 1645
VIII	3300, 3160	2265 (W)	1695, 1625
X	3430, 3300, 3170	—	1705, 1695, 1645
XI	3440, 3320 3160	—	1735, 1695, 1638

The shapes of the ultraviolet absorption spectra of II and III are similar to that of I in methanol.

It can be concluded from these spectral data that II and III possess a heptafulvene structure, both in solution and in the solid state. This conclusion is in good agreement with the results obtained by Brasen and Benson.

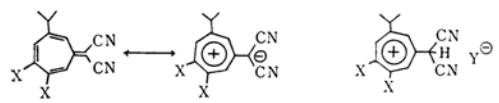
* Present address: Department of Chemistry, Tohoku University, Katahira-cho, Sendai.

1) Y. Kitahara, K. Doi and T. Kato, This Bulletin, **39**, 2444 (1966).
2) W. R. Brasen, H. E. Holmquist and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).
3) W. R. Brasen and R. E. Benson, ibid., **83**, 3135 (1961).

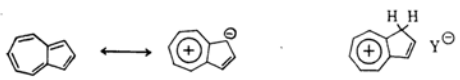
On the other hand, it has become clear that there is a large contribution of an ionic structure, quite similar to that of azulene,[4] to 8, 8-dicyanoheptafulvenes.[5]

Azulene is reported to exist as a tropylium cation in a strongly acidic medium[6,7] and the cation has been isolated as a stable crystalline salt.[8]

It may therefore, be anticipated that heptafulvenes can also exist as cations of the tropylium type in a strongly acidic medium, the cations being stabilized by amino groups at the 2 and 3 positions.



X=OCH_3
=NRR′ (R′=H, CH_3)

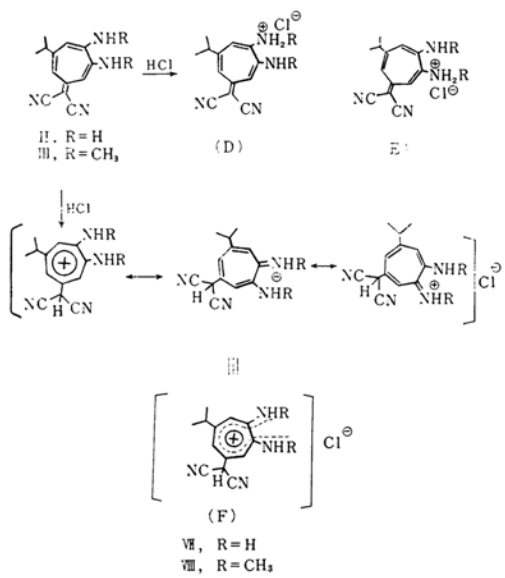


The addition of concentrated hydrochloric acid to compound II at room temperature gives a solution; after several minutes, pale yellow crystals (VII) begin to separate out. The composition of this compound corresponds to $C_{13}H_{14}N_4 \cdot HCl \cdot H_2O$, i. e., an addition product of II with one mole each of hydrochloric acid and water. Compound III also affords a yellow crystalline addition product (VIII), with one mole each of hydrochloric acid and water, i. e., $C_{15}H_{18}N_4 \cdot HCl \cdot H_2O$. Compounds VII and VIII are pale in color compared with the original compounds, II and III, suggesting that they have a different chromophore from those of II and III.

Meanwhile, when compound II or III is treated with hydrochloric acid, two ways of protonation are possible; either the protonation occurs at a nitrogen atom, forming D or E, or the dicyanomethylene groups is protonated, forming a tropylium cation (F), which is similar to the 2-aminotropoimine protonated at the imine nitrogen.

The infrared spectra of VII and VIII show a weak absorption band at 2260—2270 cm^{-1} due to a cyano group which is no longer conjugated. The ultraviolet absorption spectra of these compounds in methanol are similar to that of heptafulvene itself. In 6 N hydrochloric acid, however, they display quite different absorption maxima from those of II or III. Therefore, it can be concluded that VII and VIII have a structure similar to the hydrochloride of 2-aminotropoimine (F).

IV dissolves in 6 N hydrochloric acid, but attempts to isolate a crystalline salt analogous to VII or VIII were unsuccessful. When IV is heated in the same acid, two dimethylamino groups of IV are hydrolyzed, affording 2, 3-dihydroxy - 5 - isopropyl- 8, 8 - dicyanoheptafulvene (IX). Accordingly, the following deduction might be made; owing to the steric interference of the four methyl groups of the two adjacent dimethylamino groups, it becomes impossible for IV to form the structure corresponding to F, in which the lone paired electrons of the nitrogens and the π-electrons of the ring overlap. In a hydrochloric acid solution, IV exists as D or E, i. e., the hydrochloride of a tertiary amine maintaining the heptafulvene structure, which is hydrolyzed to IX. The above deduction is also supported by a similarity between the ultraviolet absorption spectra of IV in 6 N hydrochloric acid and in methanol.



When VII is heated in concentrated hydrochloric acid, a white crystalline compound (X), $C_{12}H_{16}O_2N_2 \cdot HCl$, is obtained, while when it is heated in methanolic hydrochloric acid, VII affords a pale yellow crystalline compound (XI), $C_{13}H_{18}O_2N_2 \cdot HCl$. X and XI are also obtained directly from II by heating it in hydrochloric acid and hydrochloric acid - methanol respectively.

In the infrared spectra of X and XI, no bands to be assigned to cyano groups are present; instead of them, bands at 1705 and 1735 cm^{-1} due to carboxyl and ester groups appear in the spectra of X and

4) A. G. Anderson, Jr., and B. M. Steckler, ibid., **81**, 4941 (1959).
5) S. Katagiri, K. Doi, Y. Kitahara and H. Azumi, This Bulletin, to be published.
6) Pl. A. Plattner, E. Heilbronner and S. Weker, *Helv. Chim. Acta*, **35**, 1036 (1952).
7) L. H. Chopard-dit-Jean and E. Heilbronner, ibid., **35**, 2170 (1952).
8) K. Hafner, *Ann.*, **625**, 108 (1959); **650**, 35 (1961).

XI respectively. The ultraviolet absorption spectra of these compounds are quite similar to that of VII in 6 N hydrochloric acid; this suggests that VII, X and XI possess the same chromophore (Fig. 1). Accordingly, it can be concluded that X and XI are both hydrochlorides of 2-aminotropoimine derivatives.

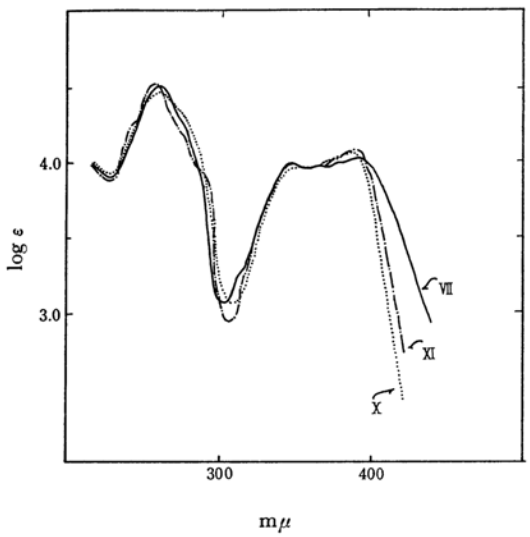
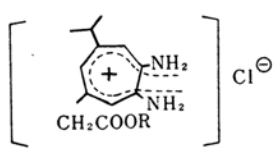


Fig. 1. Ultraviolet spectra of VII in 6 N HCl, X, XI in MeOH.

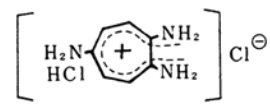
The infrared absorption spectra of these hydrochlorides, VII, X and XI are similar to each other through the whole spectral region; furthermore, they are very similar to that of the hydrochloride of 2, 5-diaminotropoimine[9] (XII) (Table II). It might, therefore, be assumed that the hydrochlorides of these compounds have similar structures.

TABLE II. IR SPECTRA OF SOME DERIVATIVES OF 2-AMINOTROPOIMINE HYDROCHLORIDES

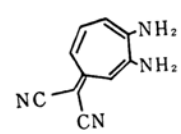
Compound	IR spectra, cm^{-1}							
VII	1590	1524	1473	1385	1365	1290	1190	1040
VIII	1590	1535	1473	1375	1350	1273	1195	1015
X	1590	1525	1472	1385	1357	1280	1196	1040
XI	1590	1522	1472	1384	1367	1300	1195	1015
XII	1590	1525	1482	1390	1350	1276	1207	1000
XIV	1595		1485	1375	1360	1295	1200	1030



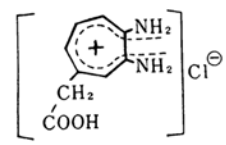
(X) R=H
(XI) R=CH_3



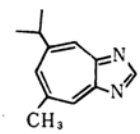
(XII)



(XIII)



(XIV)



(XV)

Similarly, on being heated in hydrochloric acid, 2, 3-diamino-8, 8-dicyanoheptafulvene (XIII) yields XIV, whose ultraviolet and infrared absorption spectra are quite similar to those of X.

When X is heated in 80% formic acid, it gives a 1, 3-diazaazulene derivative (XV).[10,11]

Experimental

2, 3-Diamino-5-isopropyl-8, 8-dicyanoheptafulvene Hydrochloride (VII).—one hundred milligrams of II were dissolved in 1 ml. of 12 N hydrochloric acid; to this solution, active charcoal* was added, and then the charcoal was filtered off. The filtrate, on standing at room temperature, deposited to give pale yellow needles, which were filtered off and washed with water to give 80 mg. of VII, m. p. 216°C (decomp.).

Found: C, 55.60; H, 5.78. Calcd. for $C_{13}H_{14}N_4 \cdot HCl \cdot H_2O$: C, 55.60; H, 6.11%.

UV λ_{max}^{MeOH} mμ (log ε): 260(4.37), 338(4.30), 408 (4.30).

$\lambda_{max}^{6\,N\,HCl}$ mμ (log ε): 263(4.51), 350(3.99), 395(4.0).

5-Isopropyl-2, 3-bis(methylamino)-8, 8-dicyanoheptafulvene Hydrochloride (VIII).—A mixture of 120 mg. of III and 1 ml. of 12 N hydrochloric acid was heated on a water bath for a short time. The mixture then turned orange. The addition of 3 ml. of water to the solution afforded 120 mg. of yellow crystals (VIII); m. p. 211—212°C (decomp.).

Found: C, 58.17; H, 6.43; N, 17.80. Calcd. for $C_{15}H_{18}N_4 \cdot HCl \cdot H_2O$: C, 58.33; H, 6.88; N, 18.11%.

UV λ_{max}^{MeOH} mμ (log ε): 243 (4.26), 338 (4.32), 430 (4.48).

9) T. Nozoe, M. Sato and T. Matsuda, *Sci. Repts. Tohoku Univ., First Ser.*, **37**, 407 (1953).
10) I. Murata, This Bulletin, **33**, 56 (1960).
11) T. Nozoe, T. Mukai and I. Murata, *J. Am. Chem. Soc.*, **76**, 3352 (1954).
* Active charcoal was found to be very effective for the purification of the hydrochlorides of 2, 3-diamino-8, 8-dicyanoheptafulvene derivatives.

$\lambda_{max}^{6\,N\ HCl}$ mμ (log ε): 280 (4.63), 358 (4.14), 420 (4.13).

When an ethanol solution of VIII was chromatographed on alumina, using ethanol as the eluting solvent, it yielded yellow crystals, m. p. 255°C (decomp.), which were identified as III by a mixed melting point determination and by a study of the infrared absorption spectrum.

The Reaction of 2, 3-Bis(dimethylamino)-5-isopropyl-8, 8-dicyanoheptafulvene (IV) with Hydrochloric Acid.—The addition of 3 ml. of 6 N hydrochloric acid to a solution of 100 mg. of IV in 3 ml. of ethanol yielded a deep red solution. To this solution a small amount of active charcoal was added, after which the mixture was heated for 30 min. in a water bath. The charcoal was then filtered off, and most of the enthanol of the filtrate was distilled off, affording a crystalline compound (50 mg.), m. p. 234°C (decomp.). An ethanol solution of this compound was treated with diazomethane in ether to yield a yellowish-orange crystalline compound, m. p. 177—178°C, which was proved to be 5-isopropyl-2, 3-dimethoxy-8, 8-dicyanoheptafulvene by a mixed melting point determination with an authentic sample and by a study of its infrared absorption spectrum.

The Reaction of 2, 3-Diamino-5-isopropyl-8, 8-dicyanoheptafulvene (II) with Methanolic Hydrochloric Acid.—a) A mixture of II (100 mg.) and 1 ml. of a 12 N hydrochloric acid-methanol (1 : 1) solution was heated on a water bath for 30 min., and then treated with active charcoal. After the charcoal had then been filtered off, the filtrate was allowed to cool to room temperature; it then gave 80 mg. of yellow prisms (XI), m. p. 221°C (decomp.), after recrystallization from a 12 N hydrochloric acid - methanol (1 : 1) mixture.

Found: C, 57.49; H, 7.09; N, 10.51. Calcd. for $C_{13}H_{18}N_2O_2 \cdot HCl$: C, 57.64; H, 7.07; N, 10.35%.

UV λ_{max}^{MeOH} mμ (log ε): 260 (4.53), 348 (3.99), 390 (4.07).

b) A mixture of II (150 mg.) and 12 N hydrochloric acid (3 ml.) was heated for 20 min., treated with active charcoal, and then filtered. After the filtrate had then been cooled, orange crystals were obtained (100 mg.), those were recrystallized from 12 N hydrochloric acid, affording needles (X), m. p. 275°C (decomp.).

Found: C, 56.31; H, 6.13; N, 10.93; Cl, 14.17. Calcd. for $C_{12}H_{16}N_2O_2 \cdot HCl$: C, 56.30; H, 6.68; N, 10.90; Cl, 13.81%.

UV λ_{max}^{MeOH} mμ (log ε): 260 (4.48), 348 (3.97), 390 (4.00).

2-Amino-4-carboxymethyltropoimine Hydrochloride (XIV).—A mixture of 120 mg. of XIII and 12 N hydrochloric acid (3 ml.) was heated for 5 min. It turned orange. After the heating had been continued at 90°C for 30 min., the solution was treated with active charcoal and the charcoal was filtered off. On cooling, white needles (XIV) (80 mg.), m. p. 270°C (decomp.), were obtained.

Found: C, 50.29; H, 4.86; N, 12.84; Cl, 16.75. Calcd. for $C_9H_{10}N_2O_2 \cdot HCl$: C, 50.35; H, 5.16; N, 13.06; Cl, 16.51%.

UV λ_{max}^{MeOH} mμ (log ε): 257 (4.40), 348 (4.00), 395 (4.04).

7-Isopropyl-5-methyl-1, 3-diazaazulene (XV).—A mixture of 220 mg. of X and 5 ml. of 80% formic acid was refluxed for one hr. The solvent was then distilled under reduced pressure, giving a red oil (XV) (100 mg.), which was then purified by chromatoraphy on alumina, using methanol as the elution solvent.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.10); 257 (4.18), 370 (3.61), 358 (3.86). Picrate: m. p. 195°C (decomp.).

Found: C, 52.15; H, 4.00; N, 16.95. Calcd. for $C_{18}H_{17}N_5O_7$: C, 52.05; H, 4.13; N, 16.84%.

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