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The Synthesis and Physical Properties of 1,6-Dimethyl-8,8-dicyanoheptafulvene

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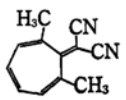
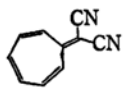
In the course of our investigation of 8,8-dicyanoheptafulvenes, we needed to prepare 1,6-dimethyl-8,8-dicyanoheptafulvene (**1**). We wish here to report the synthesis of **1** and on its abnormalities in physical properties.



(**1**)



(**2**)

According to the method of the convenient synthesis[1] of 8,8-dicyanoheptafulvenes from tropones, refluxing 2,7-dimethyltropone[2] with malononitrile in acetic anhydride gave **1** in a 17% yield upon the separation of the reaction mixture by silica-gel-column chromatography. The IR, UV, and NMR spectra showed marked changes compared to those of 8,8-dicyanoheptafulvene (**2**)[3] (*cf.* Table 1). That is, the infrared absorption of the cyano group (2225 cm^{-1}) of **1** is at a higher frequency and its intensity is relatively weaker, while the ultraviolet absorption at the longest wavelength (390 mμ) is markedly weaker in intensity and the chemical shifts of ring protons are higher than those of **2**. These observations indicate that the conjugation of the cyano group with the seven-membered ring is appreciably hindered. This hindrance could be attributed to the deviation of **1**[4] from the planarity observed in **2**[5] by X-ray analysis, a deviation resulting from the intramolecular steric interaction between the methyl and the cyano groups. This is further supported by the fact that the dipole moment, 5.68 D (in benzene at 25°C), is far smaller than the value, 6.94 D,[6] calculated by regarding the seven-membered ring as a planar and regular heptagonal.

Experimental

8,8-Dicyanoheptafulvene (2). A solution of tropone (1.125 g, 10.6 mmol) and malononitrile (1.05 g, 15.9 mmol) in 10 m*l* of acetic anhydride was heated to reflux for 1.5 hr. The volatile substances were then removed *in vacuo*, leaving reddish crystals. The crystals were collected by filtration and washed with ethyl alcohol, giving 0.860 g of **2** as orange needles. The filtrate was concentrated and chromatographed on silica-gel eluted with benzene, this provided a further 0.315 g. Total yield, 1.175 g (72%). The melting point (201—202°C) and spectral data are all identical with those of an authentic sample.

1) K. Doi and Y. Kitahara, Tohoku Local Meetings of the Chemical Society of Japan, 1959. As for the procedure, see Experimental Section.

2) N. J. Leonard, L. A. Miller and J. W. Berry, *J. Am. Chem. Soc.*, **79**, 1482 (1957).

3) T. Nozoe, T. Mukai, K. Osaka and N. Shishido, This Bulletin, **34**, 1384 (1961).

4) This was finally confirmed by X-ray analysis to be a boat form-like structure in the seven-membered ring. H. Shimanouchi, Y. Sasada, C. Kabuto and Y. Kitahara, *Tetrahedron Letters*, **1968**, 5053.

5) H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata and Y. Kitahara, This Bulletin, **39**, 2322 (1966).

6) Values of 7.49D[7] of **2** and 0.35 D of toluene were taken for the base moment and the C–CH_3 bond moment respectively.

7) M. Yamakawa, H. Watanabe, T. Mukai, T. Nozoe and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5665 (1960).

TABLE 1. IR, UV AND NMR SPECTRAL DATA

Compound	ν_{max}(KBr) cm^{-1}	λ_{max}(MeOH) mμ (log ε)	τ($CDCl_3$)
1	2225, 1612, 1580 1525, 766	245(4.04), 390(3.96)	3.43 s 4H 7.59 s 6H ($-CH_3$)
2[3]	2205, 1633, 1585 1520, 763	225(4.01), 255(4.08) 384(4.36)	2.5—3.2 m

1,6-Dimethyl-8,8-dicyanoheptafulvene (1). A solution of 2,7-dimethyltropone (1.34 g, 10 mmol) and malononitrile (0.90 g, 13.5 mmol) in 15 m*l* of acetic anhydride was heated to reflux for 45 min. The volatile substances were then removed *in vacuo*, and the red-brownish oily residue was chromatographed on silica-gel eluted with benzene. The yellow fraction collected provided 0.310 g (17%) of **1**. Recrystallization from methylene chloride - cyclohexane gave an analytical sample; yellow prisms, mp 102—103°C.

Found: C, 79.34; H, 5.69; N, 15.09%. Calcd for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38%.