

MALONONITRILE TRIMERS

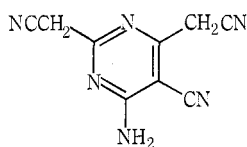
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Abstract

The structures of the malononitrile trimers I and III have been shown to be (4a) and (4e).

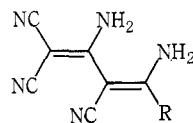
Three trimers of malononitrile were reported by Schenck and Finken¹ who designated them Trimers I, II, and III. Trimer I was obtained by treatment of an ethanolic solution of malononitrile with diethylamine. Passage of ammonia through a benzene solution of malononitrile gave Trimer II, convertible into Trimer III on pyrolysis. They suggested (1) and (2) as possible structures but did not assign them to any particular trimer.



(1)

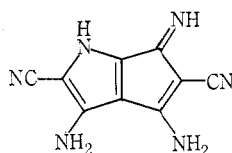
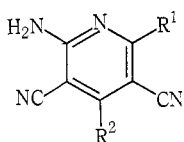


(2)

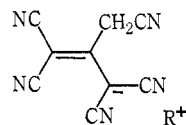


(3a) R = CH₂CN

(3b) R = CF₃



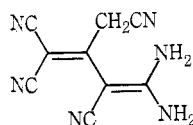
(5)



(6a) R = NH₄

(6b) R = Na

	R ¹	R ²
(4a)	CH ₂ CN	NH ₂
(4b)	Br	NH ₂
(4c)	CH(CN)CO ₂ Et	NH ₂
(4d)	CF ₃	NH ₂
(4e)	NH ₂	CH ₂ CN
(4f)	Cl	CH ₂ CN
(4g)	NHCH ₂ Ph	CH ₂ CN



(7)

On the basis of infrared spectra, Anderson *et al.*² proposed structures (1) and (3a) for Trimers II and III respectively, although they considered (1) difficult to

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¹ Schenck, R., and Finken, H., *Liebigs Ann.*, 1928, **462**, 267.

² Anderson, D. M. W., Bell, F., and Duncan, J. L., *J. chem. Soc.*, 1961, 4705.

accept chemically. From infrared and p.m.r. spectra, two Japanese groups^{3,4} considered Trimer I to have the pyridine structure (4a) arising by ring closure of (3a). However, we consider that an unambiguous distinction between such complex structures as (3a) and (4a) cannot be made on the spectral evidence reported. Junek and Sterk⁵ however proposed that (3a) is the structure of Trimer II. These latter workers also postulated the mechanistically unlikely structure (5) for Trimer III.

The only trimer whose structure has been satisfactorily elucidated is Trimer II. Taguchi and Matsuura^{3*} have shown it to be (6a) from spectral data and by synthesis from the corresponding sodium salt (6b).⁶ Alternative syntheses of Trimers I and III were obviously needed for unambiguous identification of their structures.

The bromopyridine (4b)⁷ was converted into the ethyl cyanoacetate derivative (4c) which on decarboxylation with sodium chloride in aqueous dimethyl sulphoxide⁸ gave (4a) identical with Trimer I prepared by the method of Schenck and Finken. The ultraviolet spectra of (4a) and (4b) were essentially identical and corresponded to that reported by Josey⁹ for the product from the base-catalysed condensation of malononitrile dimer with trifluoroacetonitrile. Josey assigned structure (3b) to this product, but we conclude that it should be represented as the ring-closed structure (4d).

We considered Trimer III to be the pyridine (4e) arising by protonation of (6a), attack of ammonia on a terminal nitrile to give (7), and subsequent ring closure. This was confirmed by synthesis from (4f),¹⁰ by debenzoylation of the derived benzylamine (4g) to give a product identical with Trimer III prepared by the method of Schenck and Finken.

Experimental

Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Ultraviolet spectra of solutions in 95% ethanol were measured with a Unicam SP800 spectrophotometer. Infrared spectra refer to Nujol mulls and were measured with a Unicam SP200 spectrophotometer. Proton magnetic resonance spectra were measured in (CD₃)₂SO on a Varian HA-60-IL spectrometer, and chemical shifts (δ) are given in p.p.m. relative to tetramethylsilane.

Ethyl 4',6'-Diamino-3',5'-dicyano-2'-pyridylcyanoacetate (4c)

The starting material (4b) was prepared by the method of Little *et al.*⁷ but with the use of acetonitrile as solvent. We are unable to effect the preparation in aqueous solution as reported. The product sublimed above 260° (lit.⁷ sublimed above 270°); ultraviolet spectrum: λ_{\max} 212 (ϵ 8200), 241 (35600), 249 (30000), 315 nm (5500).

* It is unfortunate that the structure of Trimer II does not appear in the abstract of the paper. We thank Dr Michiichi Taguchi, whose kindness in providing us with an English translation of his paper brought this information to our attention.

³ Taguchi, M., and Matsuura, K., *Yuki Gosei Kagaku Nyokai Shi*, 1969, **27**, 1230 (*Chem. Abstr.*, 1971, **74**, 53464p).

⁴ Takeshima, T., Yokoyama, M., Fukada, N., and Akano, M., *J. org. Chem.*, 1970, **35**, 2438.

⁵ Junek, H., and Sterk, H., *Z. Naturf. (B)*, 1967, **22**, 732.

⁶ Kelly, R. B., Slomp, G., and Caron, E. L., *J. org. Chem.*, 1965, **30**, 1036.

⁷ Little, E. L., Middleton, W. J., Coffman, D. D., Engelhardt, V. A., and Sansen, G. N., *J. Am. chem. Soc.*, 1958, **80**, 2832.

⁸ Krapcho, A. P., and Lovey, A. J., *Tetrahedron Lett.*, 1973, 957.

⁹ Josey, A. D., *J. org. Chem.*, 1964, **29**, 707.

¹⁰ Atkinson, J. D., and Johnson, M. C., *J. chem. Soc. (C)*, 1968, 1252.

Ethyl cyanoacetate (0.226 g, 2 mmol) was stirred for 10 min with a suspension of sodium hydride (50% dispersion in mineral oil, 0.15 g, 6.2 mmol) in dimethylformamide (10 ml). The bromopyridine (4b) (0.476 g, 2 mmol) was added and the resulting solution stirred at room temperature for 3 days. The mixture was diluted with water and the precipitated solid filtered off. Recrystallization from aqueous dimethylformamide gave *ethyl 4',6'-diamino-3',5'-dicyano-2'-pyridylcyanoacetate (4c) monohydrate* as white crystals (0.15 g, 28%), decomposed without melting above 250° (Found: C, 50.0; H, 4.2; N, 29.5. $C_{12}H_{10}N_6O_2 \cdot H_2O$ requires C, 50.0; H, 4.2; N, 29.2%). Infrared spectrum: ν_{\max} 3550, 3370, 3200, 2230, 1665, 1640, 1595, 1540 cm^{-1} . Ultraviolet spectrum: λ_{\max} 226 (ϵ 22500), 258 (8100), 348 nm (26300).

Decarboxylation of (4c)

A solution of *ethyl 4',6'-diamino-3',5'-dicyano-2'-pyridylcyanoacetate (4c)* (0.081 g, 0.3 mmol) and sodium chloride (0.006 g, 0.1 mmol) in water (0.011 g, 0.6 mmol) and dimethyl sulphoxide (1 ml) was heated at 130–150° for 2.5 hr. The solution was cooled, poured into water (5 ml), and the precipitated solid filtered off. Recrystallization from aqueous dimethylformamide gave *4',6'-diamino-3',5'-dicyano-2'-pyridylacetonitrile (4a)* (0.04 g, 67%), decomposed above 300° (lit.¹ decomposed above 300°). Infrared spectrum: ν_{\max} 3480, 3400, 3300, 3230, 2230, 1645, 1575, 1560 cm^{-1} . Ultraviolet spectrum: λ_{\max} 240 (ϵ 35600), 249 (27800), 317 nm (5500). P.m.r. spectrum: 4.08 (s, 2H, CH_2), 7.05 (s, 2H, NH_2), 7.42 (s, 2H, NH_2). The spectral properties were identical to those of a sample of Trimer I prepared by the method of Schenck and Finken.¹

2'-Amino-6'-benzylamino-3',5'-dicyano-4'-pyridylacetonitrile (4g)

A mixture of 2'-amino-6'-chloro-3',5'-dicyano-4'-pyridylacetonitrile (4f)¹⁰ (0.218 g, 1 mmol), benzylamine (0.107 g, 1 mmol), triethylamine (0.101 g, 1 mmol), and dimethylformamide (5 ml) was heated at 90° for 1 hr. The solution was cooled, diluted with water (50 ml), and the resulting precipitate filtered off and recrystallized from ethanol to give *2'-amino-6'-benzylamino-3',5'-dicyano-4'-pyridylacetonitrile (4g)* (0.20 g, 70%), m.p. 225–230° (dec.) (Found: C, 66.7; H, 4.5; N, 29.1. $C_{16}H_{12}N_6$ requires C, 66.7; H, 4.2; N, 29.1%). Infrared spectrum: ν_{\max} 3520, 3400, 3300, 2230, 1630, 1590, 1575 cm^{-1} . Ultraviolet spectrum: λ_{\max} 234 (ϵ 31000), 285 (22000), 342 nm (14500).

Debenzylation of (4g)

A solution of the benzylamine (4g) (0.576 g, 2 mmol) in liquid ammonia (30 ml) was treated with sodium (0.184 g, 8 mg atom) in small portions. When the addition was complete (c. 10 min), the yellow solution was stirred for 45 min and then ammonium chloride (0.43 g, 8 mmol) was added. The ammonia was evaporated off and the residue stirred with water (20 ml). The solid was filtered off and recrystallized from aqueous dimethyl sulphoxide to yield *2',6'-diamino-3',5'-dicyano-4'-pyridylacetonitrile (4e)* (0.30 g, 74%), which did not melt below 300° (lit.¹ reports failure to melt below 300°). Infrared spectrum: ν_{\max} 3500, 3400, 3280, 2230, 1655sh, 1640, 1580, 1565 cm^{-1} . Ultraviolet spectrum: λ_{\max} 227 (ϵ 20800), 278 (13100), 337 nm (7800). P.m.r. spectrum: 3.95 (s, 2H, CH_2), 7.34 (s, 4H, NH_2). The spectral characteristics were identical with those of Trimer III prepared by the method of Schenck and Finken.¹