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STERICALLY CROWDED TETRACYANO-PARA-QUINODIMETHANES: SYNTHESIS AND STRUCTURE OF 2,3,5,6-TETRAMETHYL-7,7,8,8-TETRACYANO-PARA-QUINODIMETHANE

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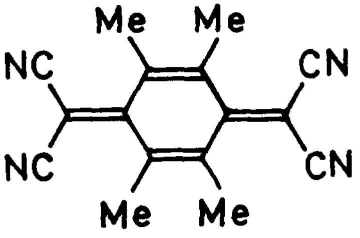
Summary: The sterically crowded 2,3,5,6-tetramethyl-7,7,8,8-tetracyano-para-quinodimethane (1) has been synthesized. The unique sterical structure of 1 is discussed based on X-ray structure analysis.

In connection with synthetic attempts to incorporate 7,7,8,8-tetracyano-para-quinodimethane (TCNQ) units into paracyclophane 1) and metacyclophane 2) systems we were interested in alternative synthetic routes suited to build up TCNQ units in a sterically crowded environment. As model system we chose the hitherto unknown 2,3,5,6-tetramethyl-7,7,8,8-tetracyano-para-quinodimethane (1).

For the synthesis of 1 we made use of two recently reported methods of preparing arylmalononitriles: (A) the copper(I)iodide-catalyzed reaction of sodio malononitrile with iodoarenes in hexamethyl phosphoric acid triamide (HMPT) 3), and (B) the reaction of lithio arylacetonitriles with 2-chlorobenzyl thiocyanate in benzene 4). Surprisingly, both reactions for preparing arylmalononitriles, to our knowledge, have not yet been used for the synthesis of TCNQ and derivatives which requires the double introduction of dicyanomethyl groups to yield 1,4-bis(dicyanomethyl)benzenes.

Syntheses of 1: 1,4-Diiodo-2,3,5,6-tetramethylbenzene 5), in analogy to procedure A 3), was converted into the bis(dicyanomethyl) compound 2 (malononitrile, sodium methoxide; CuI, HMPT; 2 h, 100°C); by oxidation of 2 (bromine, dichloromethane, water) 1 was obtained as bright yellow crystals (dec. > 250°C, 15%) 6). 1 was also prepared by reacting 2,3,5,6-tetramethylphenylene-1,4-di=



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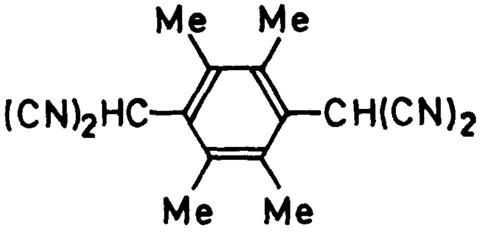

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acetonitrile [7] according to procedure B [4] (lithium diisopropylamide, benzene; 2-chlorobenzyl thiocyanate; 48 h, 20^{o}C) and subsequently oxidizing 2 (N-chlorosuccinimide, dichloromethane; 28% yield) [6].

All spectroscopic data of 1 are in agreement with the structure suggested [^{1}H-NMR (80 MHz, $CDCl_3$): δ = 2.38 (s); MS: m/z = 260 (100%, M^+); IR (KBr): ν(CN) = 2225 cm^{-1}]. In the electronic absorption spectrum (acetonitrile) 1 shows, as compared with TCNQ itself [λ_{max} = 394 nm, log ε = 4.79], a strong hypsochromic shift of the typical TCNQ absorption band to λ_{max} = 377.5 nm (log ε = 4.46); this shift is obviously the result of a deviation from planarity of the chromophoric system due to steric effects.

Molecular and Crystal Structure of 1: 1 crystallizes from acetonitrile in monoclinic prisms [space group $P2_1/n$, Z = 4; a = 771.2(1), b = 1163.9(2), c = 1584.9(3) pm, ß = 92.73(2)^{o}]. Intensity data were collected using graphite-monochromated Mo-K_α radiation and applying $\Theta/2\Theta$ technique [max. sin Θ/λ 7.6 nm^{-1}; no. of reflections measured 3596, no. of reflections with I ≥ 1.96 σ(I) 2190]. The structure was solved by direct method (MULTAN); full-matrix least-squares refinement led to R = 0.045.

The most characteristic feature of the molecular structure of 1 is the very strong deformation of the TCNQ skeleton into a boat-conformation; the planes C(1)-C(2)-C(6) and C(3)-C(4)-C(5) show an inclination against the basis plane C(2)-C(3)-C(5)-C(6) of 28.1^{o} and 30.2^{o}, respectively (fig. 1A). Bond lengths and angles are presented in fig. 1B. Comparison with corresponding bond lengths of TCNQ itself [8] show that in 1 the delocalisation of single and double bonds is significantly reduced. As a consequence of the sterical strain, too, the bond angle C(7'A)-C(7)-C(7'B) with 111.3° is smaller than in TCNQ (115.9°), and the cyano groups deviate much more from linearity (175.4°; TCNQ: (117.5°).

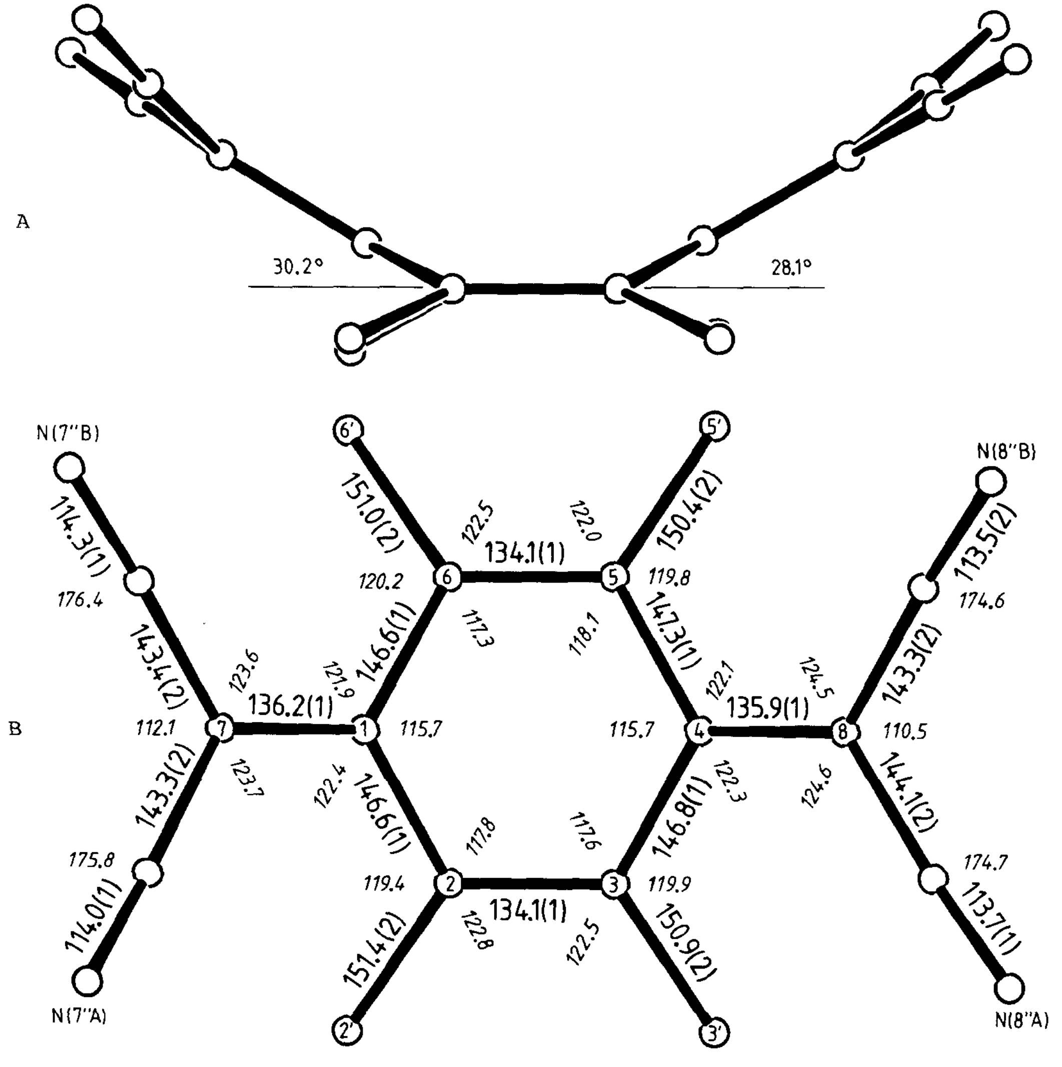

Fig. 1. Molecular structure of $\underline{\underline{1}}$: A: Side-view within the plane (C(2)-C(3)-C(5)-C(6); B: Bond lengths and angles

The crystal packing of $\underline{\underline{1}}$ (fig. 2) is strongly influenced by the bulky molecular structure of $\underline{\underline{1}}$. Whereas TCNQ crystallizes in stacks with parallel-shifted planar molecules [8] such a typical TCNQ pattern is not possible for $\underline{\underline{1}}$

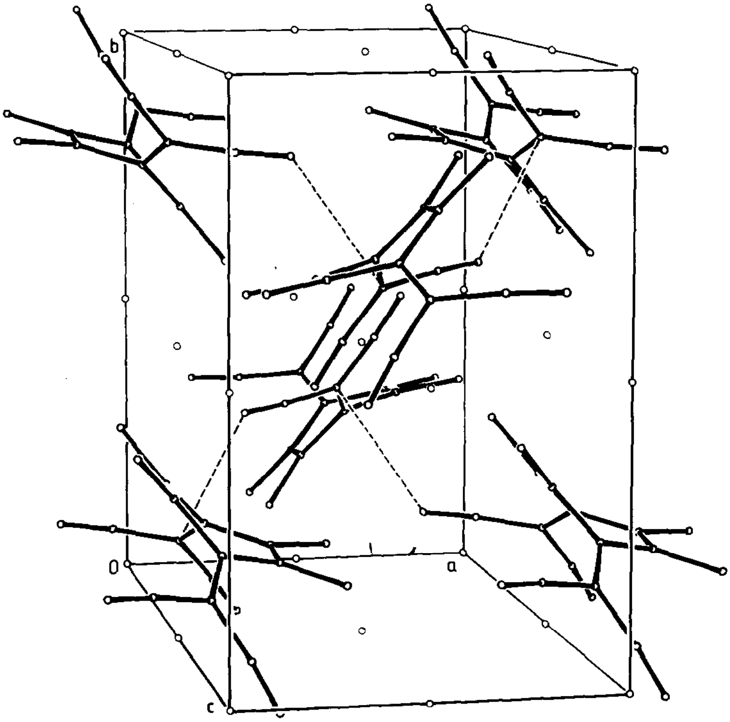

Fig. 2. Crystal packing of 1

due to its strong deviation from planarity. For the same reason 'TCNQ stacks' are also not to be expected for electron donor-acceptor complexes of 1 which are under investigation.

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