Tetrahedron Letters,Vol.27,No.21,pp 2411-2414,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

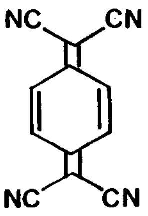
SYNTHESIS OF 29,29,30,30-TETRACYANOBIANTHRAQUINODIMETHANE

Shunro Yamaguchi*, Terukiyo Hanafusa, Takanori Tanaka, Masami Sawada,
Kozi Kondo, Masahiro Irie, Hitoshi Tatemitsu, Yoshiteru Sakata,
and Soichi Misumi

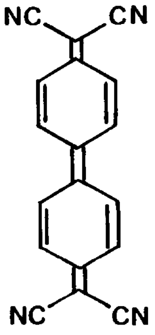
The Institute of Scientific and Industrial Research,
Osaka University, Ibaraki, Osaka 567, Japan

Summary; 29,29,30,30-Tetracyanobianthraquinodimethane (TBAQ) was prepared by the reaction of bianthrone with malononitrile in pyridine and its structure and properties were described.

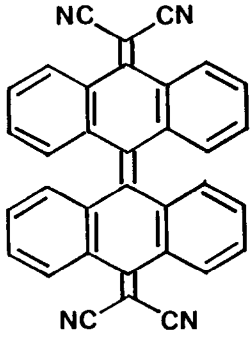
Much efforts have been made so far to develop new electron acceptors whose structures would enhance the electrical conductivities of their charge transfer complexes.1) One of the principles for designing excellent acceptors is to reduce Coulomb repulsive energies in dianion spiecies. Although such an attempt was made for the synthesis of 13,13,14,14-tetracyanodiphenoquinodimethane (TCNDQ), where two dicyanomethylene groups are far apart compared to those in TCNQ, TCNDQ has not been isolated owing to the instability of its neutral form.2) Here we report the synthesis and molecular structure of 29,29,30,30-tetracyanobianthraquinodimethane (TBAQ), a tetrabenzo derivative of TCNDQ.



TCNQ



TCNDQ



TBAQ

The synthesis of TBAQ was achieved by treatment of bianthrone with malononitrile in pyridine in a yield of 72%.3) [TBAQ: orange prisms from DMSO; mp >300°C; IR(nujol) 2220 cm^{-1}; ^1H-NMR(DMSO-d_6) 8.11, 7.51, 7.34, 7.23 ppm (ABCX pattern); Mass 480 (M^+); Elemental analysis ; Calcd for $C_{34}H_{16}N_4$: C,84.98; H,3.36; N,11.66%, Found, C,84.95; H,3.63; N,11.77%. λ_{max} in DMSO 427nm(logε 4.12), λ_{max} in DMF 423nm (logε 4.22)]. Cyclic voltammetry of TBAQ at a glassy carbon electrode in DMF shows a reduction wave at -0.70 V vs. SCE (0.2 V s^{-1} scan). The peak separation (0.05 V) indicates that two electron reduction is involved in the process. Since the solubility of TBAQ is poor to usual organic solvents as well as to DMF, no other peak is found clearly unlike bianthrone or 10,10'-dicyano-9,9'-bianthracene.4)

TBAQ was recrystallized from DMSO at 80°C to give orange prisms having a molar ratio of TBAQ:DMSO=1:2, monoclinic space group $P2_1/a$ with cell dimensions, a=8.912, b=22.390, c=8.431 Å, α=90.00°, β=90.00°, γ=107.66°, Z=2. Diffracted intensities were recorded at -78°C on a Rigaku AFC5FOS four-circle diffractometer (ω: 2θ scan, $2\theta<40°$, Mo(Kα), λ=0.71069 Å). The structure was solved by direct method (MULTAN-78),5) and refined by block-diagonal least-squares method.6) Final R-factor is 0.066 for 2097 reflections.7,8) Resulted molecular and crystal structures are shown in Figs. 1 and 2, respectively. The characteristic feature of the molecular structure of TBAQ is that the central six membered rings deform to boat shape owing presumably to steric repulsion between hydrogen atoms at peri positions and also between dicyanomethylene groups and the hydrogen atoms. The planes C(11)-C(9)-C(14) and C(12)-C(10)-C(13) make an angle of 29.8° and 35.4°, respectively. These values are larger than those of tetramethyl-TCNQ11) which deforms to similar boat form. The dihedral angles between C(11)-C(12)-C(13)-C(14) and adjacent benzene rings are 26.1° and 23.6°. These values clearly indicate that TBAQ is most sterically crowded among various TCNQ derivatives and related quinodimethanes, prepared so far.

Study of complexation of TBAQ with various donors is now under way.

Acknowledgment

The present work was supported in part by a Grant-in-Aid No. 60740275 for Scientific Research from the Ministry of Education, Science and Culture.

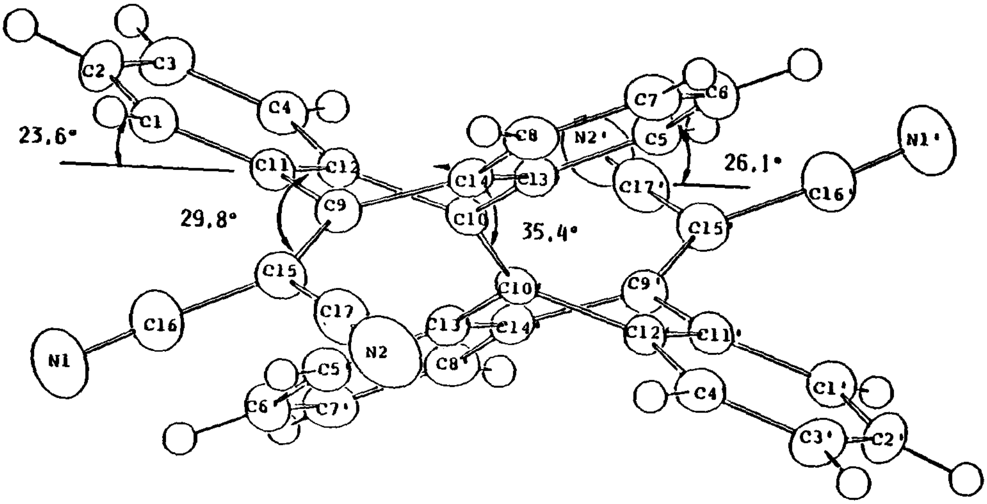


Fig. 1 Molecular structure of TBAQ 9)

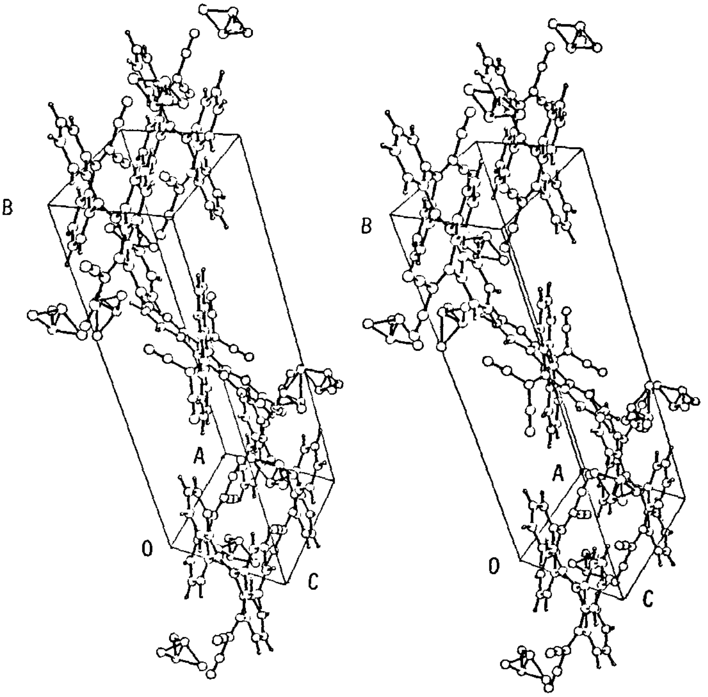


Fig. 2 Crystal structure of TBAQ 10)

References

1) R. C. Wheland and E. L. Martin, J. Org. Chem., **40**, 3101 (1975); S. Yamaguchi, H. Tatemitsu, Y. Sakata, T. Enoki, and S. Misumi, J. Chem. Soc., Chem. Commun., 1065 (1982); S. Yamaguchi, H. Tatemitsu, Y. Sakata, and S. Misumi, Chem. Lett., 1229 (1983).

2) A. W. Addison, N. S. Dalal, Y. Hayano, S. Huizing, and L. Weiler, Can. J. Chem., **55**, 4191 (1977).

3) Y. Nishizawa, T. Suzuki, Y. Yamashita, and T. Mukai, Bull. Chem. Soc. Jpn., **54**, 3601 (1985).

4) J. Heinze, Angew. Chem. Int. Ed. Engl. 202 (1981); D. H. Evans and R. W. Busch, J. Am. Chem. Soc., **104**, 5057 (1982).

5) P. Main, S. E. Full, L. Lessinger, G. Germain, J.-P. Delclercq & M. M. Woolfson, " A System of Computer Programs for the Automatic Solution of Crystal Structure from X-ray Diffraction Data, MULTAN 78", University of York (1978).

6) T. Ashida, HBLS V "The Universal Crystallographic Computing System-Osaka,", The Computation Center, Osaka University, 53 (1979).

7) Atomic scattering factors from International Tables for X-ray Crystallography; International Tables for X-ray Crystallography, Vol. 4 (1974), Birmingham, Kynoch Press.

8) All calculations were made on an ACOS-850 computer at Crystallographic Research Center, Institute for Protein Research, Osaka University.

9) ORTEP employed for drawing molecular structure; C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee (1965).

10) PLUTO78 employed for crystal structure projection; W. D. S. Motherwell, PLUTO78. Program for drawing molecular and crystal structures. University of Cambridge, England (1976).

11) B. Rosenau, C. Krieger, and H. A. Staab, Tetrahedron Lett., **26**, 2081 (1985).

(Received in Japan 18 March 1986)