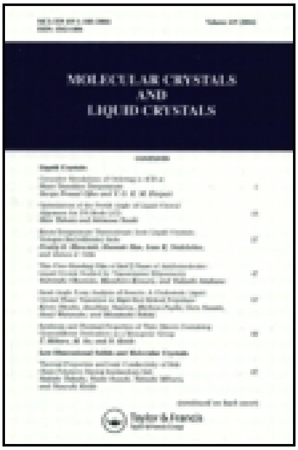

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Molecular and Crystal Structures of 2-Dicyanomethylene-1,1,3,4,5,5-Hexacyanopentenediide (DHCP) and its Tetrathiafulvalene (TTF) Complex

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Molecular and Crystal Structures of 2-Dicyanomethylene-1,1,3,4,5,5-Hexacyanopentenediide (DHCP) and its Tetrathiafulvalene (TTF) Complex

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Although the molecular structure of the cyanocarbon anion of $(C_{14}N_8)^{2-}$ had been expected as 2,3-bis(dicyanomethylene)-1,1,4,4-tetracyanobutandiide, the crystal structure analyses revealed that it has the atomic connectivity corresponding to 2-Dicyanomethylene-1,1,3,4,5,5-hexacyanopentenediide (DHCP). This stable dianion is regarded as being consisted of two dicyanomethylene groups and a planar tetracyanobutandiide. Comparing the dihedral angles between these planar parts among the different kinds of the salts, it is concluded that DHCP shows the structural flexibility. This peculiar nature is regarded as the origin to afford the characteristic molecular packing of $(TTF)_2(DHCP)(CH_3CN)$ in which the segragated stack of TTF and the donor-anion alternating stack co-exist. The salts with BEDT-TTF (ET) and BEDO-TTF (BO) showed the metallic conducting behavior down to liquid helium temperature or below.

Keywords: Organic anions; Crystal structure; DHCP; Radical ions

The chemistry of cyanocarbons had been investigated since 1958 starting from their preparation and examination of the reactivity.[1] Because of their strong electron accepting abilities and/or the stability as the anions, various kinds of charge-transfer (CT) complexes have been prepared to produce conducting and magnetic materials.[2] Recently, their ability to form the infinite chains combined with transition metals has been investigated also from the viewpoint of the crys-

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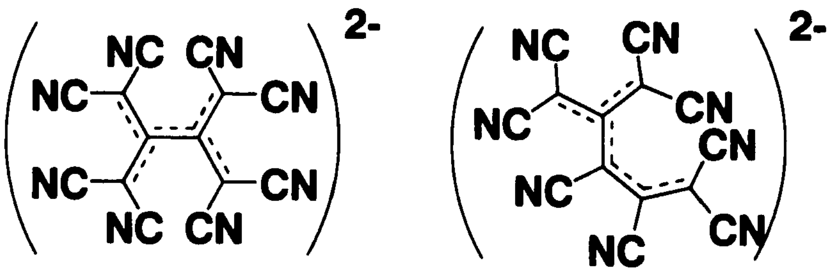
tal structure[3a] and the resultant magnetism[3b]. As for the conducting CT solids, not only the strict cyanocarbons[4] but also their heteroatom substituted derivatives have been examined[5]. It is noteworthy that dicyanamide anion which belongs to the latter category had been combined with copper(I) cation to construct the appropriate crystal structure for the 10 K class organic superconductors.[6] Since the formal charge and molecular shape are designable by the method of organic synthesis, these anions form a series of useful seeds for material sciences.

In the course of our investigation to prepare new conducting materials with the cyanocarbon anions, $(C_{14}N_8)^{2-}$ was examined. Although the chemical structure of this dianion had been assigned as 2,3-bis(dicyanomethylene)-1,1,4,4-tetracyanobutandiide (BDCTCB),[7] this work revealed the correct structure of $(C_{14}N_8)^{2-}$ as 2-dicyanomethylene-1,1,3,4,5,5-hexacyanopentenediide (DHCP). Also, the structural peculiarity of flexibility will be demonstrated to provide the information for the future use of this stable dianion.



BDCTCB^{2-} DHCP^{2-}

SCHEME 1

$(C_{14}N_8)^{2-}$ was synthesized by a slightly modified method from that reported by O.W. Webster.[7] As the counter ions, tetraalkylammonium ions (R_4N^+, R = Me, Et, Pr) were employed. In all cases, $(R_4N)_2(C_{14}N_8)$ satisfied the elemental analysis (±0.3 % for C, H, N) and showed the similar IR absorption patterns.[8,9] For the Et_4N salt which had been reported by O.W. Webster[7] as BDCTCB, spectral data were examined thoroughly and revealed to agree with that originally reported.[9]

The crystal structure analyses of $(R_4N)_2(C_{14}N_8)$ were performed on the salts of R = Me and Et.[10] Although the final R-value for the R = Et salt was not satisfactory because of the poor quality of the crystal and the incomplete modeling for

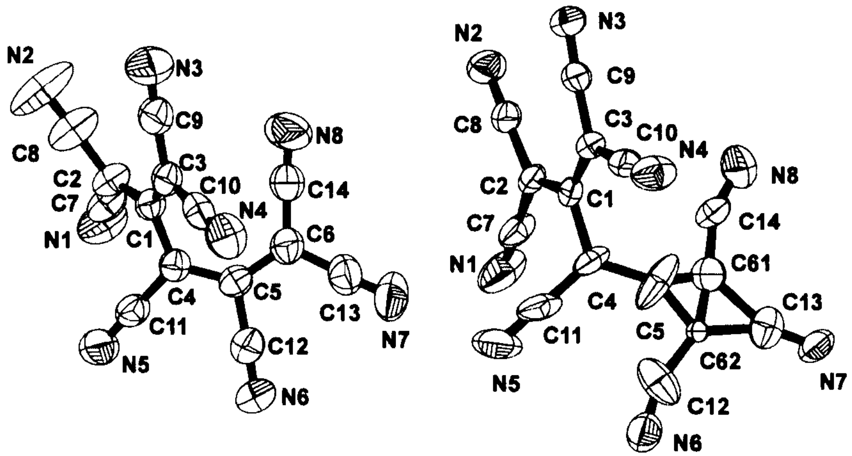


FIGURE 1 Ortep drawing of $DHCP^{2-}$ in $(Me_4N)_2(DHCP)$ (left) and in $(TTF)_2(DHCP)(CH_3CN)$ (right). In the latter, the site occupancy factors of C61 and C62 were 0.5 each

the disordered alkyl groups in Et_4N^+, both of the results of R = Me and Et showed the atomic connectivity in the dianion unambiguously. There existed only one carbon atom to which two dicyanomethylene groups were bonded (cf. Scheme 1 and Fig. 1). Hereafter, this dianion will be referred as $DHCP^{2-}$. Along with the structure in the tetrathiafulvalene (TTF) complex, the flexibility of this dianion will be described in below.

The cyclic voltammogram of $DHCP^{2-}$ showed only one irreversible oxidation peak at +1.3 V [11] which indicates that this species is stable enough as a closed shell dianion under usual oxidative conditions for the preparation of radical cation salts with donor molecules. The electrocrystallization of donor molecules was carried out in the presence of $(Et_4N)_2(DHCP)$. At present, the conductive salts with the TTF derivatives having the extended π-systems were obtained. Especially in the cases with ET and BO, the salts showed the metallic behavior down to 4.2 K or below,[12] however, the low yield of the salts and the poor quality of the crystals prevented further investigation at present.

In the case of the TTF salt, the metathesis of $(Et_4N)_2(DHCP)$ with $(TTF)_3(BF_4)_2$ provided the single crystals of $(TTF)_2(DHCP)(CH_3CN)$. Although the black block shaped crystals were insulating ($\sigma_{rt} = 10^{-7}$ Scm^{-1}) and showed the CT absorption band at higher energy region (12.3×10^3 cm^{-1}) than those of conductive salts, the quality was appropriate for the crystal structure analysis[13] and showed a unique structural feature.

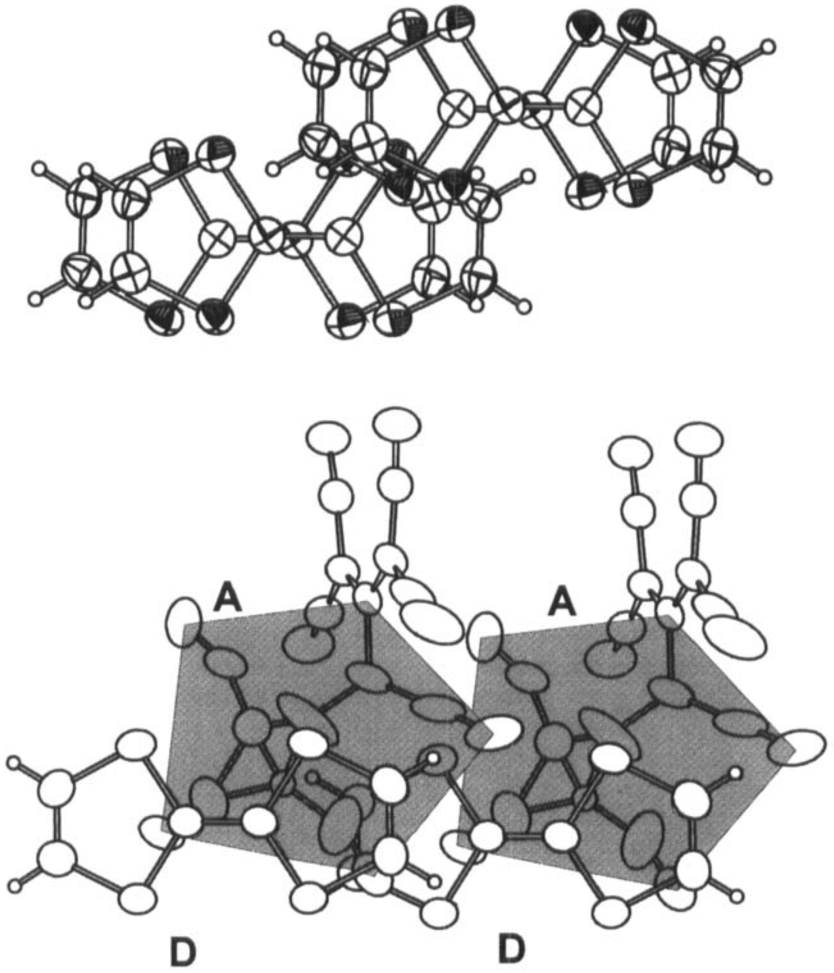


FIGURE 2 Ortep drawing of the parts of the crystal structure of $(TTF)_2(DHCP)(CH_3CN)$ projected onto a donor molecular plane. The neighboring donor dimers in a segregated column at y = 0.5 (top) and the neighboring four molecules in an alternating stack at y = 0 (bottom). In the latter, TTF and the planar part of $DHCP^{2-}$ (shaded) form the ··DADA·· type alternating stack

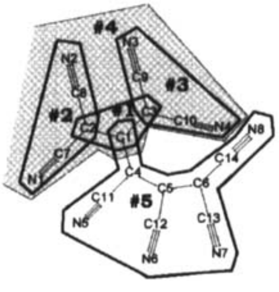
In $(TTF)_2(DHCP)(CH_3CN)$, two TTF, one DHCP dianion, and one solvent molecules are crystallographically unique. $DHCP^{2-}$ exhibits positional disorder which corresponds to C6 in Me_4N and Et_4N salts (C61 and C62 in Fig. 1). One can assign both of (N7-C13)-C61-(C14-N8) and (N7-C13)-C62-(C12-N6) as the terminal $C(CN)_2$ group.[14] This disorder indicates the rotational flexibility of the C4-C5 bond.

The bond lengths in both independent TTF molecules agreed with those in the TTF cation radical.[15] The face-to-face dimers of TTF^+ formed a segregated stack parallel to the c-axis at y = 0.5 (Fig. 2 top). The interplanar distances were 3.36 and 3.48 Å within and between dimes, respectively and the molecular overlap was rather poor in the latter case. The striking feature of the crystal structure was that this salt contained not only the segregated stack mentioned above but also the alternating stack of TTF^+ and $DHCP^{2-}$. At y = 0, the alternating stack was formed along the a-axis. As expected, only the planar part of the dianion participated in the alternating stack (Fig. 2 bottom). The dihedral angle and interplanar distance between the donor plane and the planar part of the dianion were 4.2° and 3.41 – 3.47 Å, respectively. Such a peculiar packing motif is regarded as the result from the unusual molecular shape of $DHCP^{2-}$.[16]

To demonstrate the flexibility of $DHCP^{2-}$, Table I summarizes the dihedral angles between the intramolecular planes. Each of the best plane of #2 and #3 was defined by the dicyanomethylene group at the bis(dicyanometylene)methylide group. The best plane #1 was defined by the central three carbon atoms of this substituent.

TABLE I Intramolecular Dihedral Angles of $DHCP^{2-}$ in Different Salts*

*Dihedral Angle (°)**	*Counter Component*		
	TMA	*TEA*	*TTF*
#1 – #2	12.2	15.2	1.1
#1 – #3	14.1	6.9	3.7
#2 – #3	24.9	21.3	3.6
#4 – #5	55.9	64.1	70.2



The first flexibility appeared at the dihedral angle between the planes #2 and #3. This type of flexibility had also been observed in 2-alkoxy-1,1,3,3-tetracyanoallylide (RO-TCA) anions.[17] The twisting angle varied from 3.6 to 24.9° which is smaller than those observed in RO-TCA's (8.3 – 48.4°). However, the

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* The planes #1 – #5 are defined as the best planes based on the atoms listed in below.
#1; C1, C2, C3. #2; C2, C7, C8, N1, N2. #3; C3, C9, C10, N3, N4. #4; C1, C2, C3, C7, C8, C9, C10, N1, N2, N3, N4. #5; C1, C4, C5, C6 (or C61, C62), C11, C12, C13, C14, N5, N6, N7, N8.

biggest shift from the best plane defined by all of the atoms belonging to the terminal bis(dicyanomethylene)methylide group (#4) was at most 0.71 Å (for N2 in Me_4N salt). The rest of the dicyanomethylene groups also formed a rather flat plane defined as plane #5 from which the maximum shift was 0.54 Å for C1 in the Et_4N salt. The second flexibility of $DHCP^{2-}$appeared at the dihedral angle between this plane and the plane #4, which varied from 55.9 to 70.2°. It is noteworthy that the fragment, which defines the plane #5, just corresponds to the "delocalized" part in decacyanooctatetraene dianion which is reported to show the "localized delocalization" of the π-system.[18] The last flexibility of this dianion emerged as the rotational freedom at C4 – C5 bond which was demonstrated in the TTF salt. Although the bond length of C4 – C5 (1.40(1) Å) shows the double bond character (cf. 1.489(9) Å for C1 – C4), the rotation around this bond occurred during the complex formation since the starting material of $(Et_4N)_2(DHCP)$ consisted of only one conformer. The estimation of the activation energy for this rotation is in progress.

These observations on multiple freedoms of the intramolecular rotation indicate that $DHCP^{2-}$ is rather flexible and can modify its own molecular shape according to the counter components.

Summarizing the results, this work clarified the molecular structure of $(C_{14}N_8)^{2-}$ as $DHCP^{2-}$ and proved that this dianion is flexible. The structural softness gives rise to the characteristic crystal structure of the TTF complex and also affords the metallic ET and BO salts. In the latter cases, $DHCP^{2-}$ is expected to change its conformation from that in the TTF salt to accommodate the conducting segregated column or layer of donor molecules. The peculiar structural and physical properties of the complexes with other donor molecules can be anticipated from the novel structural property of $DHCP^{2-}$, and the further complex preparations are under way.

Acknowledgements

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References

(1) T.L. Cairns, R.A. Carboni, D.D. Coffman, V.A. Engelhardt, R.E. Heckert, E.L. Little, E.G. McGeer, B.C. McKusick, W.J. Middleton, R.M. Scribner, C.W. Theobald, H.E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775–2778 (1958) and succeeding papers.

(2) W.R. Hertler, W. Mahler, L.R. Melby, J.S. Miller, R.E. Putscher, O.W. Webster, *Mol. Cryst. Liq. Cryst.*, **171**, 205–216 (1989) and references cited in.

(3) a) M. Decoster, J.E. Guerchais, Y.L. Mest, J.S. Pala, S. Triki, *Polyhedron*, **15**, 195–202 (1996); K.R. Dunbar, *Angew. Chem. Int. Ed. Engl.*, **35**, 1659–1661 (1996); S. Triki, J.S. Pala, M. Decoster, P. Molinié, L. Toupet, *Angew. Chem. Int. Ed.*, **38**, 113–115 (1999);
b) J.S. Miller, A.J. Epstein, *Chem. Commun.*, 1319–1325 (1998).

(4) a) F. Wudl, E.W. Southwick, *J. Chem. Soc., Chem. Commun.*, 254–255 (1974).
b) T. Fukunaga, M.D. Gordon, P.J. Krusic, *J. Am. Chem. Soc.*, **98**, 611–613 (1976).
c) C. Katayama, M. Honda, H. Kumagai, J. Tanaka, G. Saito, H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **58**, 2272–2278 (1985).
d) H. Yamochi, T. Tsuji, G. Saito, T. Suzuki, T. Miyashi, C. Kabuto, *Synth. Met.*, **27**, A479-A484 (1988).
e) M.A. Beno, H.H. Wang, L. Soderholm, K.D. Carlson, L.N. Hall, L. Nuñez, H. Rummens, B. Anderson, J.M. Schlueter, J.M. Williams, M.-H. Whangbo, M. Evan, *Inorg. Chem.*, **28**, 150–154 (1989).
f) W.H. Watson, A.M. Kini, M.A. Beno, L.K. Montgomery, H.H. Wang, K.D. Carlson, B.D. Gates, S.F. Tytko, J. Derose, C. Cariss, C.A. Rohl, J.M. Williams, *Synth. Met.*, **33**, 1–9 (1989).

(5) a) R.C. Wheland, J.L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916–3925 (1976).
b) H. Yamochi, K. Tsutsumi, T. Kawasaki, G. Saito, *Mater. Res. Soc. Symp. Proc.*, **488**, 641–646 (1998).

(6) a) A.M. Kini, U. Geiser, H.H. Wang, K.D. Karlson, J.M. Williams, W.K. Kwok, K.G. Vandervoort, J. E. Thompson, D.L. Stupa, D. Jung, M.-H. Whangbo, *Inorg. Chem.*, **29**, 2555–2557 (1990); J.M. Williams, A.M. Kini, H.H. Wang, K.D. Karlson, U. Geiser, L.K. Montgomery, G.J. Pyrka, D.M. Watkins, J.M. Kommers, S.J. Boryschuk, A.V.S. Crouch, W.K. Kwok, J.E. Schirber, D.L. Overmyer, D. Jung, M.-H. Whangbo, *Inorg. Chem.*, **29**, 3272–3274 (1990);
b) H. Yamochi, T. Komatsu, N. Matsukawa, G. Saito, T. Mori, M. Kusunoki, K. Sakaguchi, *J. Am. Chem. Soc.*, **115**, 11319–11327 (1993).

(7) O.W. Webster, *J. Am. Chem. Soc.*, **86**, 2898–2902 (1964). To generate the hexacyanobutadiene dianion, we used NaH of 10 times amount that reported to improve the yield of the desired product to 20 % (5 % in original paper).

(8) IR absorption patterns were compared with that reported in ref. 7 which had not given R_4N^+ bands. R = Me; The red crystals of R = Me melted at 214–216°C (IR (KBr) 2190 cm^{-1} (s), 1460(m), 1290(w), 1241(w)). The orange yellow crystals of R = Pr melted at 278°C (dec.) (IR (KBr) 2191 cm^{-1} (s), 1450 (m, shoulder), 1290(w), 1241(w)).

(9) The red crystals of R = Et melted at 209–213°C (lit. 205–211°C) and showed the following spectral data [in brackets the reported values are indicated]. IR (KBr) 2190(s), 1454 (s), 1299(w), 1240(w) [2193(s), 1453(s), 1297(w), 1239(w)], UV-Vis (in CH_3CN) 329 nm ($\varepsilon = 20230$), 420 (20290) [328 (20100), 420 (20100)].

(10) For $(Me_4N)_2(C_{14}N_8)$; triclinic, $P\bar{1}$, $a = 16.967(2)$ Å, $b = 11.6810(8)$, $c = 6.5556(9)$, $\alpha = 103.583(8)°$, $\beta = 96.11(1)$, $\gamma = 90.968(8)$, $V = 1254.6(2)$ Å^3, data were collected at room temperature, $Z = 2$, $R = 0.0787$. For $(Et_4N)_2(C_{14}N_8)$; triclinic, $P\bar{1}$, $a = 12.319(8)$ Å, $b = 13.42(1)$, $c = 11.845(9)$, $\alpha = 65.51(4)°$, $\beta = 64.78(5)$, $\gamma = 78.95(6)$, $V = 1612(2)$ Å^3, data were collected at room temperature, $Z = 2$, $R = 0.1354$.

(11) Measured in 0.1 M $(Bu_4N)BF_4$ solution in CH_3CN vs. SCE at 24°C and the scan rate of 0.2 V/sec.; under the same condition, TCNQ shows reversible redox peaks at −0.29 and 0.26 V for the oxidation processes of $TCNQ^{2-} \rightarrow TCNQ^-$ and $TCNQ^- \rightarrow TCNQ$, respectively.

(12) The donor molecules, which afforded the conductive salts were bis(ethylenedithio)-TTF (ET) (room temperature conductivity $\sigma_{rt} = 10^1 - 10^2$ Scm^{-1}), bis(ethylenedioxy)-TTF (BO) ($\sigma_{rt} = 10^2$), bis(methylenedithio)-TTF ($\sigma_{rt} = 0.5$), 3,4-ethylenedithio-TTF ($\sigma_{rt} = 10^2$), bis(vinylenedithio)-TTF ($\sigma_{rt} = 10^2$), and bis[oxybis(methylenethio)]-TTF ($\sigma_{rt} = 1$).

(13) $(TTF)_2(C_{14}N_8)(CH_3CN)$; triclinic, $P\bar{1}$, $a = 8.917(1)$ Å, $b = 21.891(3)$, $c = 8.319(1)$, $\alpha = 91.64(1)°$, $\beta = 101.13(2)$, $\gamma = 91.74(2)$, $V = 1592(1)$ Å^3, data were collected at room temperature, $Z = 2$, $R = 0.0525$.

(14) Also, the positional parameters of C5 atom may be split into two positions, though the differential synthesis afforded no peaks around C5.

(15) R. Williams, C.L. Ma, S. Samson, *J. Chem. Phys.*, **72**, 3781–3788 (1980).

(16) The co-existence of the segregated and mixed stacks in a crystal has been rarely observed. For example; Y. Yan, D.M.P. Mingos, M. Kurmoo, W.-S. Li, I.J. Scowen, M. McPartlin, A.T. Coomber, R.H. Friend, *J. Chem. Soc. Chem. Commun.*, 997–998 (1995).

(17) H. Yamochi, C. Tada, S. Sekizaki, G. Saito, M. Kusunoki, K. Sakaguchi, *Mol. Cryst. Liq. Cryst.*, **284**, 379–390 (1996); S. Sekizaki, H. Yamochi, G. Saito, *Synth. Met.*, **102**, 1711–1712 (1999).

(18) H. Yu, G. Srdanov, K. Hasharoni, F. Wudl, *Tetrahedron*, **45**, 15593–15602 (1997).