Mendeleev Commun., 1992, 2(1), 24–25

Hexacyanocyclopropane. Synthesis and Structure

Victor M. Anisimov,[a]* Alexandr B. Zolotoi,[a] Mikhail Y. Antipin,[b] Petr M. Lukin,[c] Oleg E. Nasakin[c] and Yurii T. Struchkov[b]

[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 142432 Moscow, Russia. Fax: +7 095 938 2156*

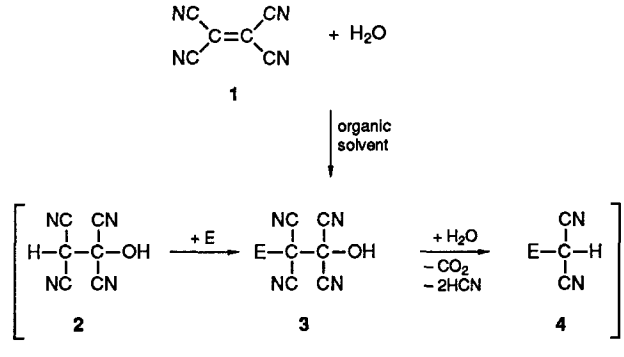
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russia*

[c] *Chuvash State University, 428015 Cheboksary, Russia*

The synthesis of hexacyanocyclopropane (HCCP) **8** has been carried out for the first time by reaction of tetracyanoethylene **1** with *tert*-butyl hypochlorite **5** in a water–1,4-dioxane system. The structure of HCCP has been determined by a single crystal X-ray diffraction study of an HCCP·3(1,4-dioxane) adduct.

The strong electron-accepting properties of cyano groups and their ability to stabilize electron-rich intermediates are known to promote nucleophilic addition at the double bond of tetracyanoethylene (TCNE). This is manifested, for example, in the excellent dienophilic capacity of TCNE in the Diels–Alder reaction.[1] However, the same properties counteract direct electrophilic addition to the central carbon atoms of TCNE.

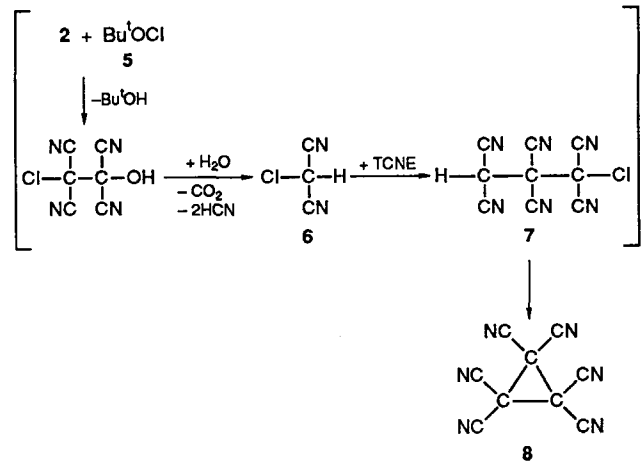
In order to extend the synthetic potential of TCNE, we have developed a method for reaction of TCNE with electrophilic reagents in a water–organic solvent (propan-2-ol, acetonitrile, dioxane, acetone, tetrahydrofuran etc.) system,[2] since TCNE is insoluble in water. The probable reaction pathway is shown in Scheme 1. According to this scheme, TCNE **1** reacts first with water, and 1,1,2,2-tetracyanoethanol **2**, thus formed, interacts with electrophile E. The reaction is accompanied by vigorous evolution of HCN and CO_2, evidently due to hydrolysis of the adduct **3**. The subsequent behaviour of the product **4** depends on the nature of the electrophile E.†



Scheme 1
E = electrophile

Using *tert*-butyl hypochlorite **5** as an electrophile in a water–dioxane system, a rapid synthesis of HCCP **8**‡§ has been carried out under mild conditions. A possible reaction pathway is shown in Scheme 2.

In accordance with the general mechanism for electrophilic addition (Scheme 1), elimination of HCN and CO_2 leads to the formation of monochloromalononitrile **6**. It should be noted that on chlorination of malononitrile only dichloromalononitrile[3] is formed, which indicates the instability and high reactivity of **6**. However, we have assumed that the lifetime of **6** is sufficiently long for it to react with TCNE. Subsequent elimination of HCl from **7** produces HCCP **8**, which forms a 1:3 crystalline adduct with dioxane and leaves the reaction phase.



Scheme 2

The structure of HCCP has been determined by a single-crystal X-ray diffraction study¶ of HCCP·3(dioxane). There are two symmetrically independent molecules in the unit cell, one (molecule A1, Fig. 1) lies in a special position on the C_3 symmetry axis, while the other (molecule A2) lies in a general position. As the structural parameters of molecules A1 and A2 are, in fact, equivalent, only molecule A1 and its environment will be considered below.

The C–C bond length of 1.51 Å in unsubstituted cyclopropane[4] is shorter by 0.02 Å than that in ethane. The $(NC)_2C$–$C(CN)_2$ carbon–carbon bond lengths in 2,5-diphenyl-3,3,4,4-tetracyanopyrrolidone[5] with eclipsed cyano groups and that in 1,1,2,2-tetracyanoethane[6] are 1.598(3) Å and 1.562(1) Å, respectively. The cyclopropane carbon–carbon bond length in A1 is 1.530(6) Å, *i.e.*, as in unsubstituted cyclopropane there is a tendency for the C—C bond to be short in the three-membered ring of HCCP.

In HCCP one might expect conjugation of the cyano groups with the cyclopropane π-system, which would result in a shortening of the C—CN bond and an elongation of the —C≡N bonds. However, these bond lengths in HCCP, taking into account their effective shortening by 0.02 Å due to thermal

† A paper reporting studies with E = PhN_2Cl, HNO_2 and TCNE is in preparation.

‡ *Synthetic procedure*: After addition of 0.02 mol Bu'OCl to a suspension of 0.01 mol TCNE in 25 ml 1,4-dioxane, the suspension was cooled to +5 °C, and 25 ml water was added dropwise. The reaction is complete on precipitation of a 1:3 crystalline adduct of HCCP with dioxane. The reaction temperature should be held at <10 °C. On recrystallisation from dioxane and removal of dioxane and water, VHCCP was isolated as a white, polycrystalline powder, stable for storage, but very hydrolysable, in 55% yield.

§ *Spectroscopic data for* **8**: IR (Vaseline) ν_{max}/cm^{-1} 2290, 2250, 2220 (C≡N); ^{13}C NMR (CD_3CN, 22.63 MHz) δ 106.24 (C≡N).

¶ *Crystal data* for **8**: $C_{21}H_{24}N_6O_6$, M = 456.5, rhombohedral, space group $R3c$, $a = b = 20.443(3)$ Å, $c = 39.712(3)$ Å, $\gamma = 120.0°$, $Z = 24$, $V = 14372.8$ Å^3, $\rho_c = 1.27$ Mg m^{-3}, $F(000) = 5760$, $R = 0.041$ ($R_w = 0.037$) for 1821 independent reflections with $I > 2\sigma(I)$ from 4724 reflections measured at 163 K, θ–2θ scan, $(\sin\theta/\lambda)_{max} = 0.63$, λ(Mo–Kα) = 0.71069 Å, graphite monochromator, Siemens P3/PC diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares in anisotropic approximation (isotropic for H atoms). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, *J. Chem. Soc., Chem. Commun.*, 1992.

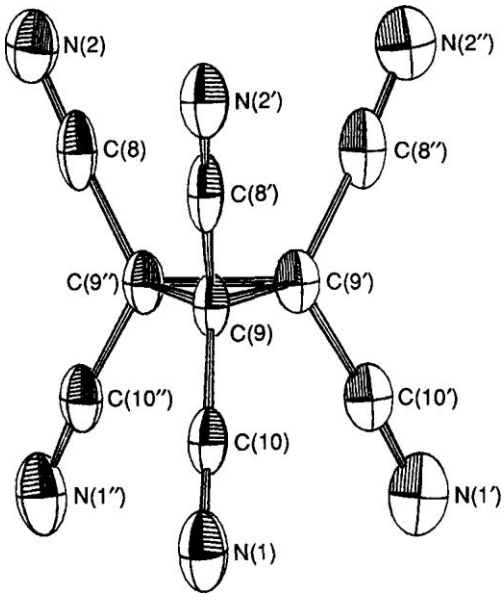


Fig. 1 The HCCP molecule A1. The primed and double primed atoms are related to the reference atoms by $-y, x-y, z$ and $-x+y, -x, z$ symmetry operations, respectively.

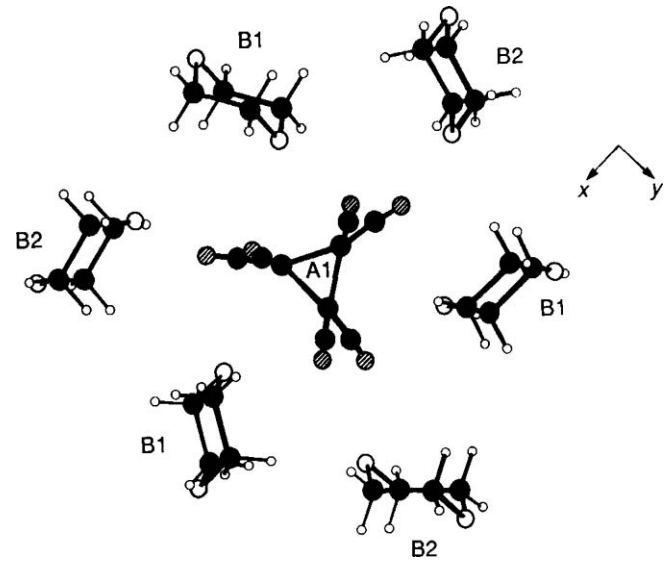


Fig. 2 Projection onto the $x0y$ plane, showing the HCCP molecule A1 surrounded by dioxane molecules (B1, B2). The dioxane oxygen atoms are situated in the plane of the cyclopropane carbon atom ring. (●) carbon, ( ) nitrogen, (○) oxygen, (○) hydrogen.

vibration of the terminal atoms in the cyano groups, correspond to standard values for C—CN and —C≡N bond lengths measured in acetonitrile.[4] This fact may be considered to result from either the absence of a conjugation effect or the existence of other effects with opposing structural consequences, which override the influence of conjugation.

In the structure of HCCP the cyano groups are distorted from linearity by approximately 5°, with all the nitrogen atoms of the cyano groups being displaced to one side of the molecular C_3 symmetry axis (Fig. 1). This bending of the C—C≡N fragment appears to be due to electronic factors, since MNDO optimization of the corresponding bond angles in an isolated HCCP molecule reproduces the experimental results.

In the crystal, each HCCP molecule is surrounded only by dioxane molecules (Fig. 2), forming two kinds of intermolecular contacts. These are A1—B1, where the dioxane oxygen atom has slightly shortened contacts of 2.90 Å with two cyclopropane carbon atoms, and A1—B2, where the oxygen atom has a short contact of 3.20 Å with two of the carbon atoms of the geminal cyano groups. Molecule A2 forms similar but slightly shorter (by 0.05–0.10 Å) C···O contacts. Both kinds of contacts are favourable for interaction of the dioxane oxygen lone pairs with the π-orbitals of the cyano groups and the cyclopropane π-system. All N···H and C···C contacts are close to the sums of the van der Waals radii of the corresponding atoms.[7]

Received: Moscow, 19th July 1991
Cambridge, 11th October 1991; Com. 1/03775G

References

1 A. J. Fatiadi, *Synthesis*, 1987, 749.
2 A. B. Zolotoi, V. M. Anisimov, P. M. Lukin and A. N. Lyshchikov, to be published.
3 A. Freeman, *Chem. Rev.*, 1969, **69**, 591.
4 L. V. Vilkov, V. S. Mastryukov and N. I. Sadova, *Opredelenie geometricheskogo stroeniya svobodnykh molekul.* (Determination of the geometrical structure of free molecules) Khiniya, Leningrad, 1978 (in Russian).
5 A. B. Zolotoi, A. N. Lyshchikov, P. M. Lukin, A. I. Prokhorov, O. E. Nasakin, A. Kh. Bulai and L. O. Atovmian, *Dokl. Adad. Nauk SSSR*, 1990, **313**, 110 [*Dokl. Chem.* (*Engl. Transl.*), 1990, **313**, 186].
6 J. P. Declerq, *Acta Crystallogr., Sect. C*, 1983, **39**, 1401.
7 Yu. V. Zefirov and P. M. Zorki, *Zh. Strukt. Khim.*, 1976, **17**, 994 [*J. Struct. Chem.* (*Engl. Transl.*), 1976, **17**, 581].