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Weak C—H$\cdots$N$\equiv$C hydrogen bonds in the structures of two poly(cyano)-substituted ring systems

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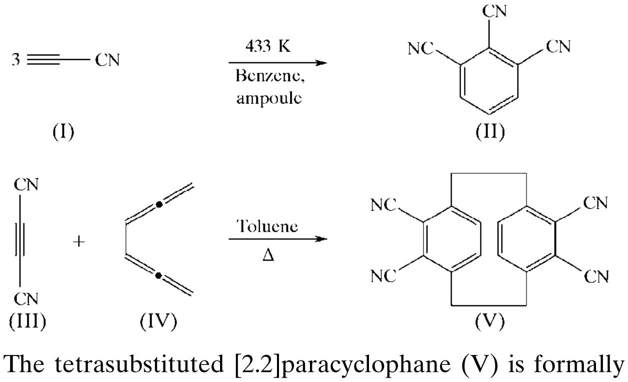
In benzene-1,2,3-tricarbonitrile, $C_9H_3N_3$, the packing of the two independent molecules is three-dimensional and complex, involving *inter alia* bifurcated $(C—H)_2\cdots N$ systems from neighbouring CH groups. In [2.2]paracyclophane-4,5,12,13-tetracarbonitrile, $C_{20}H_{12}N_4$, the [2.2]paracyclophane systems display the usual distortions, namely lengthened C—C bonds and widened sp^3 angles in the bridges, narrow angles in the six-membered rings at the bridgehead atoms, and flattened boat conformations of the rings. The molecules are linked by a series of C—H$\cdots$N interactions to form layers parallel to the *ab* plane.

Comment

Heating cyanoacetylene, (I), at 433 K results in the formation of 1,2,4- and 1,2,3-tricyanobenzene, (II); we have shown that this trimerization involves the intermediate generation of tricyano-Dewar benzenes (Witulski *et al.*, 1990). We now report the crystal structure of (II). For the 1,2,4 isomer, we have so far been unable to obtain crystals of X-ray quality.



The tetrasubstituted [2.2]paracyclophane (V) is formally a dimer of phthalonitrile, in which the two aromatic halves are held in fixed orientation by the ethano bridges. Considering that the monomer is, for example, the starting material for phthalocyanines, dimer (V) should also show interesting chemical behaviour. Having prepared (V) many years ago (Hopf & Lenich, 1974), we now report its structure. Since compounds (II) and (V) display similar C—H$\cdots$N$\equiv$C interactions in the molecular packing, we present the structures together.

Compound (II) crystallizes with two independent molecules in the asymmetric unit (Fig. 1); these are, however, essentially identical. The molecular dimensions are as expected. The interplanar angle between the two molecules is 68.43 (6)°.

The main interest centres on the molecular packing. Reddy *et al.* (1995) have shown for 1,3,5-tricyanobenzene, the only other tricyanobenzene for which an X-ray structure analysis has been performed, that the packing is determined by weak C—H$\cdots$N$\equiv$C hydrogen bonds (Desiraju & Steiner, 1999) that in projection give a pseudo-hexagonal pattern. Each H$\cdots$N interaction is simultaneously part of both bifurcated

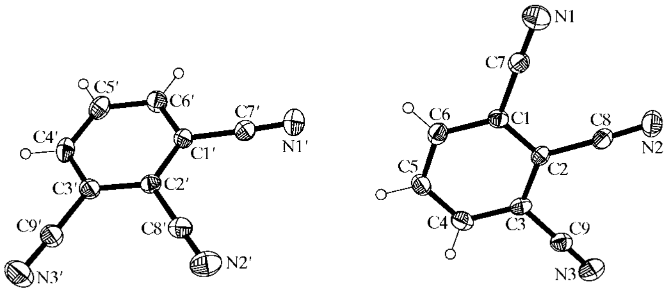


Figure 1
The two independent molecules of (II). Displacement ellipsoids represent 50% probability levels.

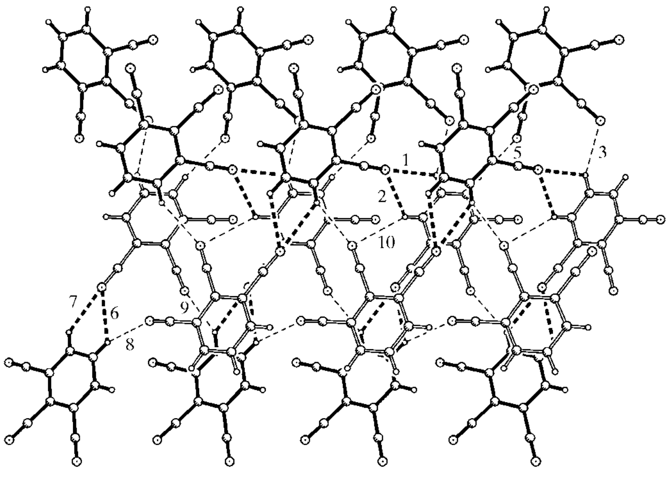


Figure 2
The packing of (II), viewed parallel to the *b* axis in the region $z \simeq 0$ (bottom) to $z \simeq \frac{5}{8}$ (top). Molecules generated from the second independent molecule (atom labels with primes) are drawn with open bonds. Hydrogen bonds (see *Comment* and Table 1) are indicated by dashed lines; one of each independent hydrogen bond is numbered according to the order of Table 1, but they do not correspond to the asymmetric unit as defined in the coordinate list. The positioning of the labels is based on the space available in the figure; it is not possible to label all interactions for a given molecule without loss of clarity. Hydrogen bond 4 is not included in this view.

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(two H-atom donors to the same acceptor) and three-centre (one H-atom donor to two acceptors) hydrogen-bond systems; each H atom donates to two N atoms, and each N atom accepts two H-atom donors. The packing of (II), as might be expected in space group $P2_12_12_1$ and with two independent molecules, is three-dimensional and complicated, but a reasonably comprehensible overview can be obtained (Table 1 and Fig. 2) in terms of C—H···N interactions; there are no C—H···(ring centroid) contacts shorter than 3.49 Å.

Molecule 1 occupies the regions at $z \simeq 0, \frac{1}{2}$, *etc*., and forms layers connected by hydrogen bond 4 (numbering according to the order in Table 1) *via* the 2_1 screw axis parallel to *a*. Molecule 2 occupies the regions $z \simeq \frac{1}{4}, \frac{3}{4}$, *etc*., and forms layers connected by hydrogen bond 10 *via* the 2_1 screw axis parallel to *b*. The main interest thus involves the interplay in the region at $z \simeq \frac{3}{8}$, which is shown in Fig. 2; nine of the ten independent hydrogen bonds can be accommodated in this view.

The neighbouring CH groups C5—H5 and C6—H6 in both molecules form bifurcated hydrogen bonds to atom N1 of the other molecule; these (hydrogen bonds 6 and 7, and 1 and 2) are shown as thicker bonds in Fig. 2, and one such system (6/7) is implicitly recognizable in Fig. 1. In both molecules, atom H4 forms one reasonably linear hydrogen bond (4 and 5), whereas atoms H5 and H6 participate in rather nonlinear but two-centre hydrogen bonds (8 and 9, and 3 and 10) in addition to the bifurcated interactions. The (uncorrected) hydrogen-bond length limit H···N has to be set at *ca* 2.9 Å to find all the interactions; this seems to be normal for the analysis of C—H···N≡C systems (*e.g.* Reddy *et al*., 1995). The correct compromise between the use of high or low contact radii, which may lead, respectively, either to a mass of unimportant detail or to an apparent lack of significant contacts, is not always easy to find.

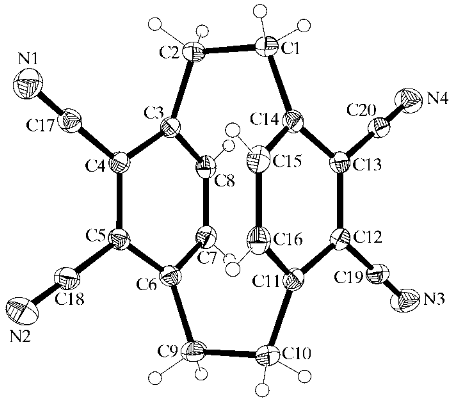

Figure 3
The molecule of (V). Displacement ellipsoids represent 50% probability levels.

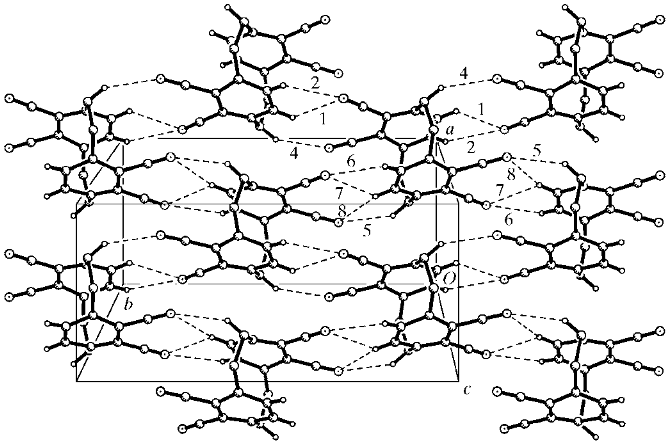

Figure 4
The packing of (V), viewed perpendicular to the *ab* plane in the region $z \simeq \frac{1}{4}$. Hydrogen bonds are indicated by dashed lines, drawn thicker for the bifurcated systems, and are numbered for one molecule according to their order in Table 3, but they do not correspond to the asymmetric unit as defined in the coordinate list. H atoms not involved in hydrogen bonds have been omitted. Hydrogen bond 3 is not included in this view.

The acceptor properties of the N atoms differ. Atoms N1 and N1′ accept only the bifurcated interactions, atoms N2 and N3′ each accept one branch of a three-centre system, atom N2′ accepts one branch from each of two three-centre systems, and atom N3 accepts the two linear two-centre interactions. The topological difference between the two independent molecules is thus established.

The molecule of compound (V) (Fig. 3) has no imposed symmetry, but its noncrystallographic symmetry is close to $2/m$ (the r.m.s. deviation of the non-H atoms is 0.034 Å). The molecular dimensions are largely as expected; in particular, the usual distortions of [2.2]paracyclophanes are observed (lengthened C—C bonds and widened sp^3 angles in the bridges, narrow angles in the six-membered rings at the bridgehead atoms, and flattened boat conformation of the rings; Table 2).

Despite the more complicated nature of the molecule of (V), the molecular packing is conceptually much simpler than that of (II). It involves layers parallel to the *ab* plane, in which N atoms act as acceptors for weak C—H···N≡C hydrogen bonds (Table 3 and Fig. 4; hydrogen-bond numbers in Fig. 4 correspond to the order of Table 3). It is noteworthy that hydrogen bonds 5, 6, 7 and 8 form a concerted system of bifurcated and three-centre bonds; hydrogen bonds 1 and 2 form a further bifurcated system. As for (II), some of the contacts involve long H···N distances (up to 2.9 Å uncorrected), but their striking combined effect is that of a series of intermolecular links roughly parallel to the *b* axis. Only the contact H1*B*···N2^{ii} (hydrogen bond 3) is not observed within the layers; instead, it serves to connect the layers. There are no C—H···(ring centroid) contacts shorter than 3.18 Å.

Experimental

Compound (II) was prepared from cyanoacetylene, (I), as previously described (Witulski *et al.*, 1990); the spectroscopic and analytical data were consistent with those reported previously. Single crystals were obtained by slow cooling from carbon tetrachloride. Cyclophane (V) was prepared as described by Hopf & Lenich (1974) by the cycloaddition of dicyanoacetylene, (III) (Hopf, 1995), to 1,2,4,5-hexatetraene, (IV) (Hopf *et al.*, 1981). All spectroscopic and analytical data agreed with those reported in the literature (Hopf & Lenich, 1974). Single crystals were obtained from acetonitrile.

Compound (II)

Crystal data

$C_9H_3N_3$
M_r = 153.14
Orthorhombic, $P2_12_12_1$
a = 6.7083 (12) Å
b = 7.8650 (14) Å
c = 28.811 (5) Å

V = 1520.1 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 133 (2) K
0.23 × 0.15 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
17402 measured reflections

2581 independent reflections
2067 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.089

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.115
S = 1.07
2581 reflections

217 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.32 e Å^{-3}

Table 1
Hydrogen-bond and short-contact geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5′—H5′···N1$^{\rm i}$	0.95	2.71	3.320 (3)	123
C6′—H6′···N1$^{\rm i}$	0.95	2.64	3.288 (3)	125
C5′—H5′···N2$^{\rm ii}$	0.95	2.55	3.380 (3)	146
C4—H4···N3$^{\rm iii}$	0.95	2.63	3.566 (3)	169
C4′—H4′···N3$^{\rm iv}$	0.95	2.60	3.528 (3)	167
C5—H5···N1′	0.95	2.64	3.262 (3)	124
C6—H6···N1′	0.95	2.65	3.261 (3)	123
C5—H5···N3′$^{\rm v}$	0.95	2.57	3.430 (3)	150
C6—H6···N2′$^{\rm vi}$	0.95	2.78	3.650 (3)	154
C6′—H6′···N2′$^{\rm vii}$	0.95	2.89	3.758 (3)	152

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$; (v) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (vi) $x-1, y, z$; (vii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Compound (V)

Crystal data

$C_{20}H_{12}N_4$
M_r = 308.34
Monoclinic, $P2_1/n$
a = 7.0277 (6) Å
b = 15.1197 (14) Å
c = 14.3219 (14) Å
β = 103.603 (4)°

V = 1479.1 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 133 (2) K
0.40 × 0.22 × 0.12 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
16873 measured reflections

4321 independent reflections
3137 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.130
S = 1.06
4321 reflections

217 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.22 e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (V).

C1—C2	1.5877 (15)	C9—C10	1.5856 (15)
C14—C1—C2	112.60 (8)	C5—C6—C7	116.37 (9)
C3—C2—C1	112.28 (8)	C16—C11—C12	116.70 (9)
C4—C3—C8	116.84 (9)	C15—C14—C13	116.57 (9)

Table 3
Hydrogen-bond and short-contact geometry (Å, °) for (V).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···N1$^{\rm i}$	0.95	2.69	3.3654 (15)	129
C7—H7···N1$^{\rm i}$	0.95	2.90	3.4710 (15)	120
C1—H1*B*···N2$^{\rm ii}$	0.99	2.50	3.3569 (15)	145
C2—H2*B*···N2$^{\rm i}$	0.99	2.55	3.4380 (15)	149
C10—H10*A*···N4$^{\rm iii}$	0.99	2.60	3.4606 (15)	145
C15—H15···N3$^{\rm iii}$	0.95	2.78	3.4221 (15)	125
C16—H16···N3$^{\rm iii}$	0.95	2.82	3.4403 (15)	124
C16—H16···N4$^{\rm iii}$	0.95	2.90	3.7133 (15)	145

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

H atoms were included, starting from calculated positions, using a riding model with C—H distances of 0.95 (aromatic) and 0.99 Å (CH_2). $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent C atom. Compound (II) crystallizes by chance in a chiral space group, although the molecule is achiral. In the absence of significant anomalous scattering, Friedel opposite reflections were merged.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3057). Services for accessing these data are described at the back of the journal.

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