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Molecular Tapes based on C≡N···Cl Interactions

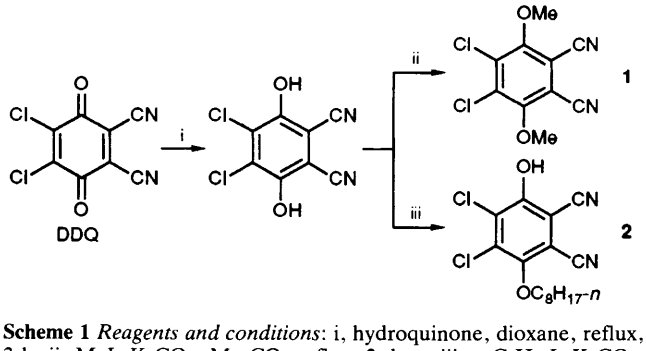
D. Shekhar Reddy,[a] Kaliyamoorthy Panneerselvam,[a] Tullio Pilati[b] and Gautam R. Desiraju*[a]

[a] *School of Chemistry, University of Hyderabad, PO Central University, Hyderabad 500 134, India*
[b] *Dipartimento di Chimica Fisica ed Elettrochimica e Centro CNR, Università di Milano, 20133 Milano, Italy*

Weak C≡N···Cl interactions may be used to design linear molecular tapes.

The construction of molecular ensembles, utilising the directional characteristics of intermolecular forces, is one of the key elements of contemporary supramolecular chemistry.[1] Linear or zig-zag arrays of flat molecules have been described by Lehn[2] and by Whitesides[3] who has referred to such arrays as 'molecular tapes'. Tapes, such as those found in the crystal structures of molecular complexes of substituted aminopyrimidines or melamines and substituted barbituric acids,[2,3] have been designed using the directional properties of strong N–H···O bonds.[4,5] The underlying rationale is that these bonds are so specific and important in crystal packing that molecular assembly can proceed in a regular, anticipated manner. In this communication, we show that molecular tapes may be constructed with forces that are far weaker than conventional hydrogen bonds.

Short C≡N···Cl contacts were first postulated by Hassel[6] and later reviewed by Britton.[7] We have shown that N···Cl distances, D, in crystals range between 3.00 and 3.45 Å and that C≡N···Cl angles, θ, vary between 80 and 180°.[8] This C≡N···Cl contact arises owing to the polarisability of Cl, and the crystal packing of several simple chloro cyano compounds, for example the polymorphs of 4-chlorobenzonitrile, may be understood on the basis of a secondary motif built up *via* these $C{\equiv}N^{\delta-}\cdots Cl^{\delta+}$ interactions. Accordingly, it was felt that substituted 2,3-dicyano-5,6-dichlorobenzenes would be good candidates for the formation of a C≡N···Cl mediated molecular tape such as is shown in Fig. 1. Compounds **1** [crystals from $CHCl_3$, m.p. 187 °C, IR(KBr) ν/cm^{-1} 2890, 2220, 1450, 1360, 1210; ^{1}H NMR ($CDCl_3$) δ 4.1 (s, 6H); MS (*m/z*, %) 256 (M^+, 59%) ($C_{10}H_6Cl_2N_2O_2$), 241 (100%) (M−Me), 231 (50%) (M−CN)] and **2** [crystals from 1 : 1 AcOH–CCl_4, m.p. 115 °C, IR (KBr) ν/cm^{-1} 3400, 2900, 2250, 1580, 1460, 1200; ^{1}H NMR (CD_3COCD_3) δ 3.95 (t, 2H), 1.80 (m, 2H), 1.35 (m, 10H), 0.90 (t, 3H); MS (*m/z*, %) 342 (5%) ($C_{16}H_{18}Cl_2N_2O_2$), 228 (15%) (M−C_8H_{16}), 112 (80%) (C_8H_{17})] were therefore synthesised from DDQ and their crystal structures determined.



Scheme 1 *Reagents and conditions*: i, hydroquinone, dioxane, reflux, 3 h; ii, MeI, K_2CO_3, Me_2CO, reflux, 3 days; iii, *n*-$C_8H_{17}I$, K_2CO_3, Me_2CO, reflux, 1 day

A view of the crystal structure of the dimethoxy derivative **1** is shown in Fig. 2.† The molecule is bisected by a twofold axis and [010] translated molecules are related by very short C≡N···Cl contacts [D = 3.099(5) Å, θ = 137.5(4)°]. In this structure, crystallographic symmetry dictates that the tape is perfectly flat and undistorted, there being no offset of molecules within, or perpendicular to, the molecular planes. The three-dimensional structure is generated by tape stacking (plane-to-plane perpendicular distance, 3.665 Å) and by close packing of adjacent methoxy groups.

A stereoview of the crystal structure of the hydroxy octyloxy derivative **2** is shown in Fig. 3.† Here too, the tape structure is intact, though there is a slight in-plane (lateral) offset; the C≡N···Cl contacts though longer [D = 3.404(3) Å, θ = 146.1(2)°; D = 3.458(3) Å, θ = 132.4(2)°] are prominent. As in the case of other weak intermolecular interactions (C–

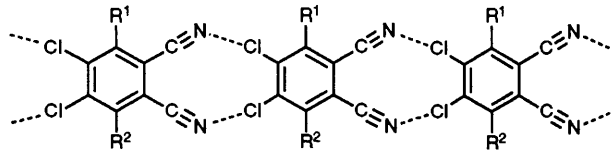


Fig. 1 Schematic view of the molecular tape formed with C≡N···Cl interactions

† *Crystal data* for **1**: $C_{10}H_6N_2O_2Cl_2$, M = 257.08, monoclinic, *C2/c*, a = 16.46(1), b = 9.11(2), c = 7.33(1) Å, β = 93.24(8)°, V = 1097(3) Å^3, Z = 4, F(000) = 520.0, D_c = 1.556 Mg m^{-3}, μ(Mo-Kα) = 5.13 cm^{-1}, crystal mosaicity high, T = 293 K, 760 non-zero (3σ) reflections out of 921 collected with 2 < 2θ < 50°, solution SHELXS-86, refinement SHELX-76, R = 0.073, R_w = 0.085, C, N, O, Cl anisotropic, H isotropic.

Crystal data for **2**: $C_{16}H_{18}N_2O_2Cl_2$, M = 343.10, orthorhombic, *Pbca*, a = 47.023(3), b = 9.424(1), c = 7.607(2) Å, V = 3371(2) Å^3, Z = 8, F(000) = 1424.0, D_c = 1.345 Mg m^{-3}, μ(Mo-Kα) = 3.43 cm^{-1}, T = 293 K, 1969 non-zero (3σ) reflections out of 2654 collected with 2 < 2θ < 55°, solution SHELXS-86, refinement SHELX-76, R = 0.034, R_w = 0.035, C, N, O, Cl anisotropic, H isotropic.

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.

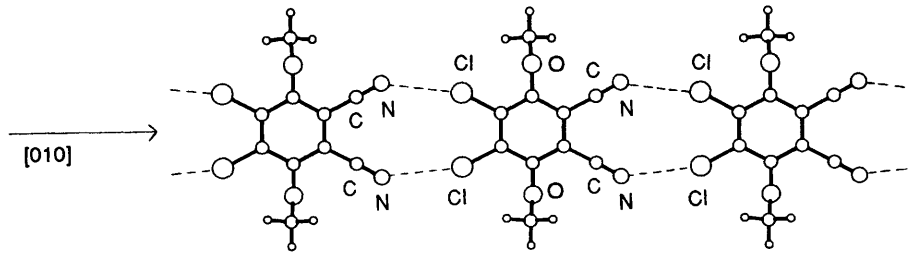


Fig. 2 Molecular tape in the crystal structure of 2,3-dicyano-5,6-dichloro-1,4-dimethoxybenzene **1**

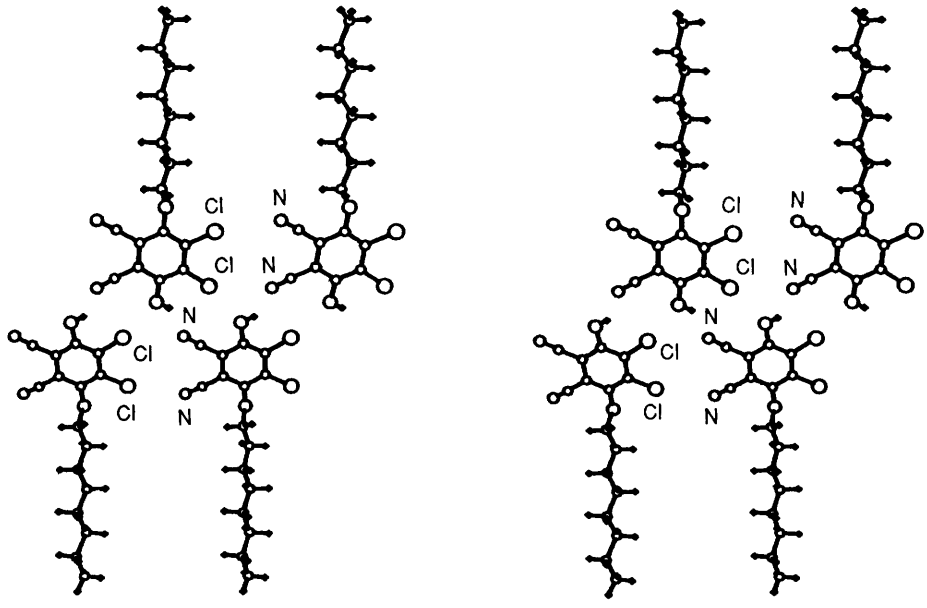
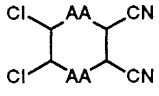


Fig. 3 Stereoview of the crystal structure of 2,3-dicyano-5,6-dichloro-4-octyloxyphenol **2** to show the tape structure, C≡N···Cl and C≡N···H–O contacts. Other molecules (not shown here) are arranged so that close packing of the alkyl chains is achieved.



X

H···O, Cl···Cl, Br···O *etc.*) the length of the contact seems less important than its directional properties. It is noteworthy that the tape, which is assembled with relatively weak C≡N···Cl interactions is sufficiently robust in the presence of stronger C≡N···H–O hydrogen bonds [N···O = 2.795(3) Å, N···H–O = 144.0(3)°] and hydrophobic interactions involving the octyloxy tails.

This C≡N···Cl molecular tape seems to be a new structural motif in crystals. A survey of the Cambridge Structural Database[9] revealed eight compounds containing the archetypal fragment **X**, where AA is any atom and the cyclic bond types are any combination of single, double or aromatic bonds. However, the tape motif discussed here does not occur among these eight structures which include DDQ and six of its molecular complexes. Presumably because quinone packing modes are more specific,[10] these seven compounds do not show the tape pattern.‡ It must be mentioned that a molecular tape of the kind discussed here is present in the crystal structure of 2,3-dicyano-5,6-dichloropyrazine.[11] This structure shows similarities to the structures of compounds **1** and **2**.[12] It was expected that the tape motif would also occur in the crystal structure of 5,6-dichloro-2,3-dicyano-1,4-dioctyloxybenzene. However, our attempts to prepare this compound from the monooctyloxy derivative **3** were unsuccessful.

‡ The final retrieved structure is tetrachlorophthalonitrile, BAWMUH, which also does not show the tape motif.

Our results show that a relatively weak interaction, such as C≡N···Cl, may be utilised reliably to design supramolecular structures, possibly in the presence of stronger forces. It is likely that analogous C≡N···Br and C≡N···I mediated molecular tapes may be similarly constructed.

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