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A molecular salt of tricyanomethanide anion and a *N,N'*-dianisylphenazinium dication: cooperative affects of methoxy⋯methoxy and C≡N⋯N⁺ intermolecular contacts

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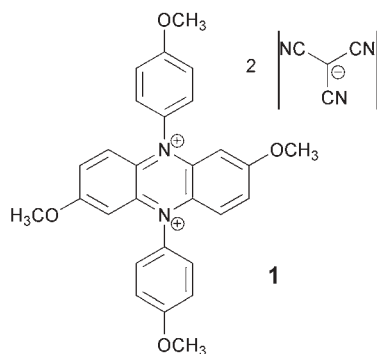
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A molecular salt of tricyanomethanide anion and a *N,N'*-dianisylphenazinium dication forms extended supramolecular assemblies that consist of unusual methoxy⋯methoxy and C≡N⋯N⁺ intermolecular contacts.

Since collections of non-bonded contacts influence the formation of molecular crystals, it is not surprising that identifying the recognition profile of individual chemical functions attached to a variety of chemical frameworks remains an active topic of materials research. One possible indication of progress realised in this area is the direct use of information gathered from fundamental studies of supramolecular synthons to the development of materials with practical functions.^{1–4} The list of notable applications^{5,6} of crystal engineering continues to grow and serves as motivation for future work. Another area of developmental importance is the search for new supramolecular synthons. Although a path less trodden, investigations that seek to uncover new venues of intermolecular contacts provide a valuable resource by adding to the current understanding of structural features responsible for crystal cohesion. Most additions to the extant database of molecular interactions often occur serendipitously, and thus progress in this area is measured by small, usually unmethodical, advances. Herein we report the surprising structure of molecular salt **1** formed from tricyanomethanide (TCM) and a phenazinium dication.



Our recent investigations of the crystal packing behavior of the *N*-oxide group have demonstrated the importance of N–O[−]⋯donor interactions as a structural tool for bimolecular assembly.^{7–10} Due to the strong hydrogen bond acceptor ability of the N–O[−] group, we have successfully generated cocrystalline assemblages with a variety of organic donors. The present work reports one such investigation. However, unlike our previous studies where cocrystallization resulted in bimolecular arrays constructed from the expected fundamental building-blocks, the current study revealed a surprising chemical transformation resulting from low-temperature cocrystallization of an equimolar mixture of dianisyl nitroxide and tetracyanoethylene (TCNE). This transformation of TCNE to TCM has been previously reported in the literature.¹¹ Spectroscopic and crystallographic† investigations of the sample obtained from this slow evaporation process showed **1** as the product.

Inspection of the crystal structure of **1** revealed a blend of unusual non-bonded contacts. As shown in Fig. 1, the structure of **1** is constructed from a 1 : 2 ratio of *N,N'*-dianisylphenazinium and TCM ions positioned on inversion and two-fold symmetry operators, respectively. The conformation of the phenazinium dication is planar with the pendant orthogonal *p*-anisyl groups (C3–N1–C7–C8 = 80.23°) covalently attached to each N⁺ atom. Closer inspection of the pyrazinium core reveals bond distances and angles consistent with an aromatic species (C–N⁺_{ave} = 1.394(4) Å; sum of C–N1⁺–C angles = 359.9(2)°).^{12,13} The planar TCM anion possesses local C_{2v} symmetry with a central sp² hybridized trivalent C16 atom.

Each phenazinium dication is associated with neighboring TCM anions *via* C15=N2⋯N1⁺ electrostatic interactions (N2⋯N1⁺ = 3.172(3) Å; C15=N2⋯N1⁺ = 147.6(2)°) as shown in Fig. 2. This motif propagates in the crystal to form catemeric molecular chains. Although the two symmetry related cyano groups are involved in the construction of this motif, the third cyano group (C17=N3) lacks any discernable intermolecular close contacts within van der Waals radii. Another interesting structural feature of **1** is the occurrence of methoxy⋯methoxy connections (C13⋯O1 = 3.187(3) Å; O1–C13⋯O1 = 157.7(2)°). These apparent attractions appear to further stabilize the structure and result in 2-D molecular networks in the *ac* plane (Fig. 3).

The observed phenazinium⋯TCM and methoxy⋯methoxy packing motifs prompted us to explore the frequency of these patterns and their potential usefulness as supramolecular synthons. Surprisingly, a search of the CSD¹⁴ (version 5.26 with August 2005) failed to uncover any additional structures with the phenazinium⋯TCM motif. Closer inspection of the retrieved

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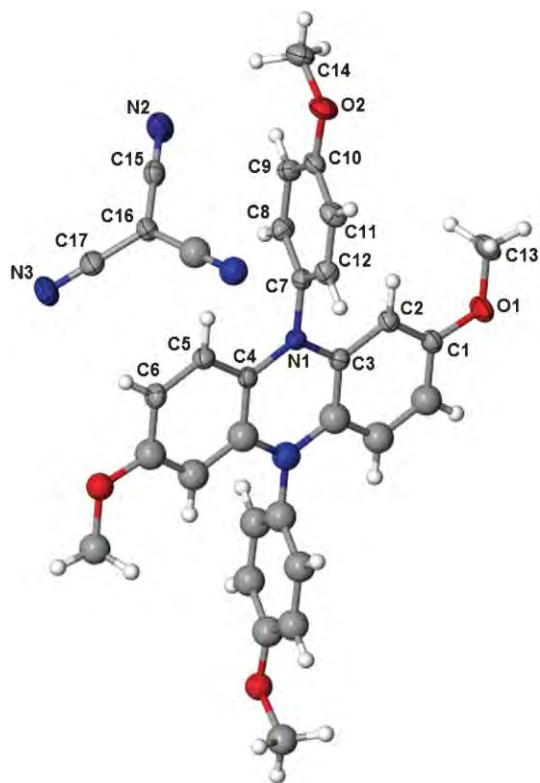


Fig. 1 The molecular structure and labeling scheme of **1** showing 50% probability displacement ellipsoids for the asymmetric unit.

structures only revealed two additional examples with the pyrazinium dication core (DAYBIO and JUXLAP) and five structures with the TCM anion (AMCYME, CUQZAP01, KADGUR01, SEJJUM, TOKXIA). Only in the case of the ammonium salt of TCM (AMCYME) are $C\equiv N\cdots N_{sp^3}$ contacts observed ($N\cdots N^+ = 2.924\text{--}3.080\text{ \AA}$).

Although the methoxy \cdots methoxy interaction has been previously reported in the literature,^{15–17} to our knowledge the degree of motif persistence and preferred geometry of this pattern remains relatively undiscovered. Inspection of the the CSD resulted in 97 organic structures (217 fragments) consisting of anisyl groups with intermolecular methoxy \cdots methoxy contacts less than the sum of van der Waals radii (3.22 Å; ref. 18). Fig. 4 shows a correlation plot of this interaction with a significant concentration of data

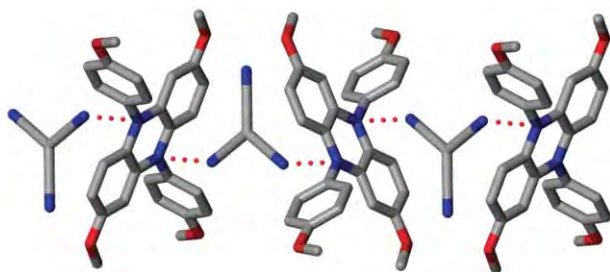


Fig. 2 View of the molecular packing of **1** projected down the a axis showing $C\equiv N\cdots N^+$ interactions. Intermolecular contacts depicted as dotted lines. Symmetry codes: $i -x, y, 5/2 - z$; $ii \ 1/2 - x, 1/2 - y, 2 - z$.

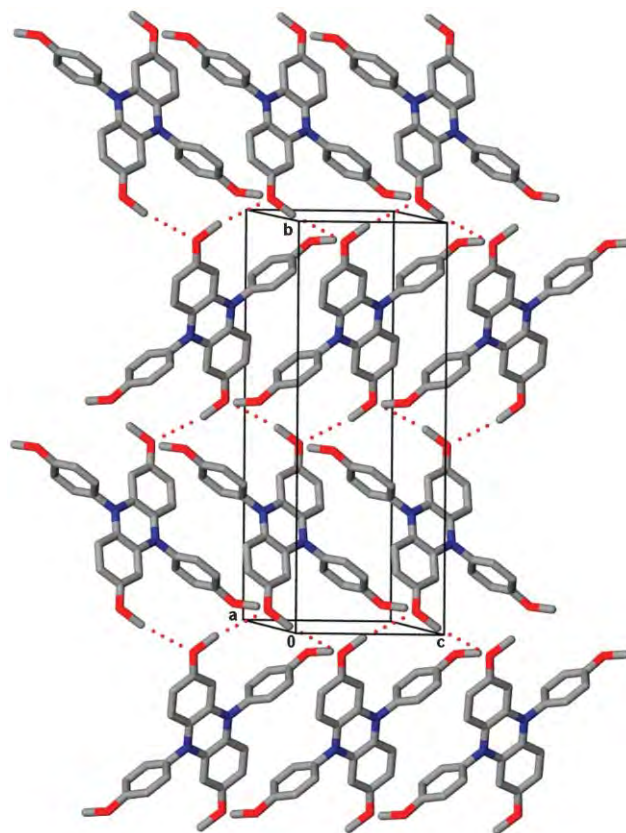


Fig. 3 View of the molecular packing of **1** showing methoxy \cdots methoxy interactions. TCM molecules removed for clarity. Symmetry codes: $i \ x, 1 - y, 1/2 + z$, $ii \ x, 1 - y, z - 1/2$.

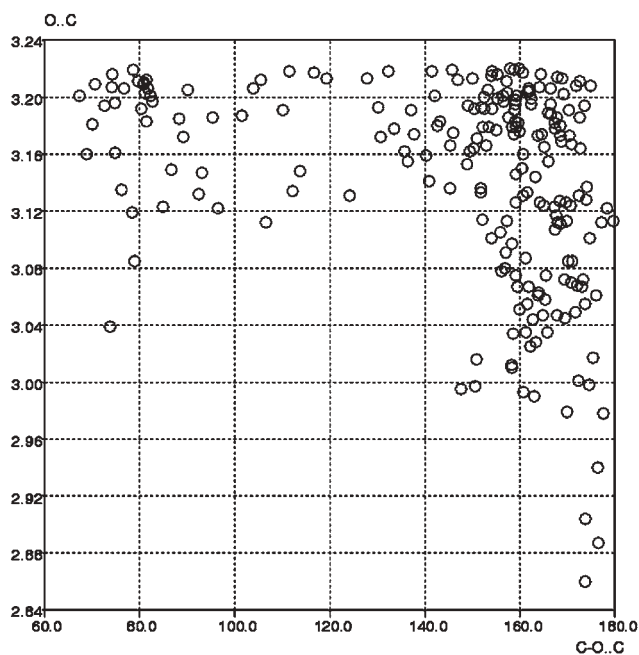


Fig. 4 Correlation plot of the intermolecular bond distances and angles of anisyl methoxy \cdots methoxy contacts retrieved from the CSD.

(27%) near $140 \leq \text{O} \cdots \text{O} \leq 180^\circ$ and $2.84 \leq \text{C} \cdots \text{O} \leq 3.12 \text{ \AA}$ favoring a linear alignment of methoxy \cdots methoxy contacts. These data provide compelling evidence for the alignment of methoxy groups which would appear to originate from complementary attractive forces rather than just the consequence of close packing.

While the catalog of known non-bonded contacts continues to increase each year, one must wonder how many additional useful supramolecular synthons remain to be discovered? This structural study draws attention to the need for exploration of new or less recognized intermolecular contacts that may be practically useful in controlling the geometry of molecular arrays. In the case of **1**, little or no information is known about the organizational behavior of the methoxy \cdots methoxy or phenazinium \cdots TCM interactions. Additional work is necessary to realize the structural preferences and transferability of $\text{C} \equiv \text{N} \cdots \text{N}^+$ and methoxy \cdots methoxy motifs as viable supramolecular building-blocks for future supramolecular studies.

Notes and references

† Crystal data for **1**: $\text{C}_{32}\text{H}_{26}\text{N}_5\text{O}_4$, $M = 544.58$, monoclinic, space group $C2/c$, $a = 16.4791(9) \text{ \AA}$, $b = 21.8079(12) \text{ \AA}$, $c = 7.8598(4) \text{ \AA}$, $\beta = 104.85(3)^\circ$, $V = 2730.2(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.325$, $\mu(\text{Mo-K}\alpha) = 0.090 \text{ mm}^{-1}$, $T = 173 \text{ K}$. 2497 unique reflections ($R_{\text{int}} = 0.034$). Final $R_1 [1834 I > 2\sigma(I)] = 0.0574$, wR_2 (all data) = 0.1652. CCDC reference number 290608. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516674h. *Synthesis*: To a 10 mL round-bottom flask was added 0.050 g (0.22 mmol) of dianisyl amine and 3 mL of a 1 : 1 methylene chloride : acetone solution. To this was added 0.1624 g (0.23 mmol) of oxone. The heterogeneous mixture was stirred vigorously at room temperature under nitrogen for 4 h and to the resulting dark solution was added 50 mL of diethyl ether and 50 mL of hexane. Dianisyl nitroxide was collected as a red-purple solid (0.25 g, 0.10 mmol, 46%). An equimolar ratio of dianisyl nitroxide and tetracyanoethylene was dissolved in acetonitrile. The dark

purple solution was placed in the freezer (-5°C) with ether diffusion and after several days afforded dark purple plate-like crystals of **1**.

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