Molecular Compounds and Complexes.
XII.† The Ternary Charge-Transfer Salt Pyridinium–1-Naphthylamine–Picrate (Kofler's Ternary Complex)

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Abstract

The ternary charge-transfer salt pyridinium–1-naphthylamine–picrate is monoclinic, $a = 21.035$ (2), $b = 11.545$ (2), $c = 8.514$ (2) Å, $\beta = 98.10$ (2)°, $Z = 4$, $P2_1/a$. The structure was refined to $R = 0.121$, with 2049 counter intensities. There is an unusual centrosymmetric arrangement of six moieties (pyridinium... 1-naphthylamine...picrate... 1̄...) stacked plane-to-plane. The two such groups in the unit cell have their stack axes approximately perpendicular and are linked by hydrogen bonds between pyridinium NH^+ and phenolic O^-. The pyridinium and picrate ions are ordered, but the 1-naphthylamine molecule apparently takes up a number of orientations within its plane; these could not be specified with certainty. The crystallographic evidence for proton transfer corroborates earlier conclusions drawn from IR spectroscopy. There is also a charge-transfer interaction between the 1-naphthylamine and picrate moieties, corroborating earlier conclusions drawn from the electronic spectra of the crystals.

Introduction

Ternary π–π^* charge-transfer molecular compounds are rare (Herbstein, 1971); their number becomes even smaller if one excepts those where the third component does not participate in the charge-transfer interaction [*e.g.* benzidine–TCNQ.1.8CH$_2$Cl$_2$ (Ikemoto & Kuroda, 1968), benzidine–TCNQ.benzene (Yakushi, Ikemoto & Kuroda, 1974), benzidine–TNB.0.5 benzene (Yakushi, Tachikawa, Ikemoto & Kuroda, 1975),
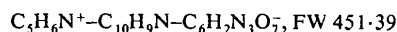
and D,L-tryptophan–picrate.methanol (Gartland, Freeman & Bugg, 1974)]. Indeed, the structure of only one authentic π–π^* ternary CT compound appears to be known [3,3′-dimethylthioazolinocarbocyanine–TCNQ–9-dicyanomethylene-2,4,7-trinitrofluorene (Kaminskii, Shibaeva & Atovmyan, 1974)]. Thus the structure of Kofler's (1944) ternary compound of 1-naphthylamine, picric acid and pyridine is of considerable interest, especially as conclusions have been drawn from IR and visible spectral studies (Matsunaga & Saito, 1972) regarding the respective roles of proton and charge transfer in this molecular compound. The present investigation confirms these conclusions and shows that the ternary compound has an unexpected and unusual arrangement of the components.

Experimental

Preparation of the crystals

Red prisms of the ternary compound (elongated along [101]) were grown from a pyridine solution containing equimolar amounts of 1-naphthylamine and

† Part XI: Herbstein, Kapon, Rzonzew & Rabinovich (1978).

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Table 1. *Crystal data*

$C_5H_6N^+$–$C_{10}H_9N$–$C_6H_2N_3O_7^-$, FW 451.39

Monoclinic	Space group $P2_1/a$
$a = 21.035$ (2) Å	$D_m = 1.463$ Mg m^{-3*}
$b = 11.545$ (2)	$D_c = 1.454$ for $Z = 4$
$c = 8.514$ (2)	$F(000) = 936$
$\beta = 98.10$ (2)°	μ(Cu $K\alpha$) = 0.960 mm^{-1}
$V = 2047.0$ Å^3	λ(Cu $K\alpha_1$) = 1.54051 Å
Chemical analysis (wt%, meas./calc.)	C 56.20/55.88 H 3.87/3.79 N 15.64/15.51

* Flotation in aqueous KI solution.

picric acid. The crystals are unstable in the atmosphere and were sealed into Lindemann-glass capillaries. Crystal data are given in Table 1; cell dimensions were determined from 15 reflections with $48\cdot6 < 2\theta < 85\cdot3°$ (Cu $K\alpha$ radiation).

During this work, crystals of pyridinium picrate and 1-naphthylamine–picric acid were also obtained. The former were identical to the material studied by Talukdar & Chaudhuri (1976); the latter (yellow-brown needles elongated along [001], had $a = 17\cdot02$, $b = 7\cdot34$, $c = 15\cdot88$ Å, $\beta = 126°$, $D_c = 1\cdot54$ Mg m^{-3} for $Z = 4$, density not measured, space group probably $P2_1/c$, but the presence of a screw axis was not definitely established because of poor crystal quality. The mean reflection intensity decreased rapidly with increased $\sin\theta/\lambda$. The compound 2(1-naphthylamine)–picric acid, reported by Matsunaga & Saito (1972), was not encountered by us.

Measurement of intensities

The intensities of 2959 reflections ($\sin\theta/\lambda \le 0\cdot55$ Å^{-1}) were measured on a Syntex $P\bar1$ four-circle diffractometer (graphite-monochromated Cu $K\alpha$, $\omega/2\theta$ method, variable scan speed according to prescan of peak intensity, $\Delta\omega = 0\cdot5°$, background measured at peak extremities). 910 reflections had $F_o < 2\cdot5\sigma(F_o)$ and were classed as unobserved. Intensities were corrected for Lp factors but not for absorption.

Solution of the crystal structure

This was effected via MULTAN (Germain, Main & Woolfson, 1971). The E values were calculated from the molecular scattering factors of pyridine, 1-
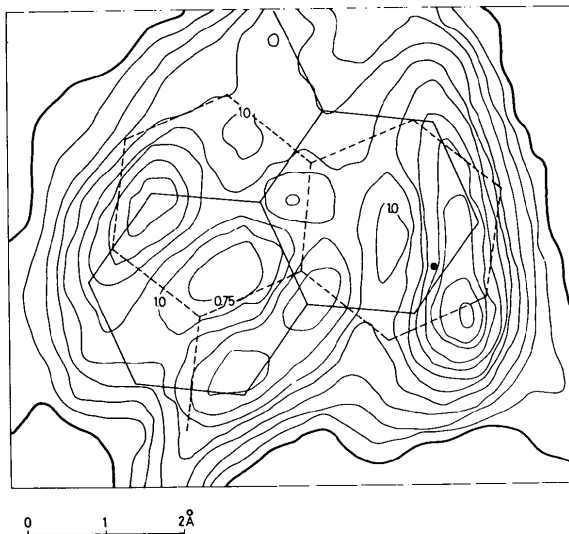

Fig. 1. Difference synthesis in the plane of the 1-naphthylamine molecule; contours are at intervals of 0·25 e Å^{-3}, with the zero contour accentuated. Two possible orientations of the molecule are shown, that represented by full lines being indicated in Fig. 2.

naphthylamine and picric acid (Main, 1976). 350 reflections with $E > 1\cdot54$ were used and the solution with the highest combined figure of merit (2·604) was correct. The E map showed the pyridinium and picrate moieties clearly (the evidence for the proton transfer is discussed below); in the region between these two ions, 10 small peaks were found which did not conform to the shape expected for 1-naphthylamine and which suggested that this molecule was disordered.

The parameters of the pyridinium and picrate moieties were refined by least squares and convergence was reached at $R = 0\cdot121$, goodness of fit $= 4\cdot25$ (observed reflections only); for all reflections $R = 0\cdot137$. The structure factors included contributions from a 1-naphthylamine molecule located in the plane between the pyridinium and picrate moieties. A difference synthesis calculated at this stage showed six H atoms attached to the pyridine ring (i.e. including the proton transferred from the picric acid) and appreciable electron density in the plane of the 1-naphthylamine, suggesting that this molecule had not been

Table 2. *Atomic coordinates* ($\times10^4$) *for non-hydrogen atoms*; PC = *picrate*, PY = *pyridinium*, NA = 1-*naphthylamine*

The coordinates for NA are for the orientation shown as full lines in Fig. 1.

	x	y	z
PC C(1)	3898 (3)	9664 (5)	199 (7)
PC C(2)	4195 (3)	10257 (6)	1602 (7)
PC C(3)	4766 (3)	9958 (7)	2496 (8)
PC C(4)	5074 (3)	8985 (7)	2016 (7)
PC C(5)	4829 (3)	8306 (6)	748 (8)
PC C(6)	4240 (3)	8638 (5)	−158 (6)
PC N(2)	3875 (4)	11283 (5)	2149 (7)
PC N(4)	5680 (3)	8627 (8)	2944 (9)
PC N(6)	4002 (3)	7893 (5)	−1435 (7)
PC O(1)	3409 (2)	10058 (4)	−608 (5)
PC O(21)	3290 (3)	11218 (5)	2224 (7)
PC O(22)	4209 (3)	12075 (5)	2608 (9)
PC O(41)	5895 (3)	9205 (8)	4095 (8)
PC O(42)	5956 (3)	7760 (7)	2515 (8)
PC O(61)	4309 (3)	7064 (5)	−1723 (7)
PC O(62)	3492 (3)	8070 (5)	−2200 (7)
PY N(1)	2421 (2)	4770 (4)	3293 (9)
PY C(1)	2439 (3)	5651 (6)	4329 (8)
PY C(2)	2928 (3)	5710 (6)	5549 (7)
PY C(3)	3408 (3)	4839 (7)	5692 (8)
PY C(4)	3374 (3)	3965 (6)	4589 (9)
PY C(5)	2873 (3)	3947 (5)	3413 (8)
NA C(1)	3194 (10)	5560 (14)	175 (12)
NA C(2)	3756 (13)	4796 (18)	311 (25)
NA C(3)	4316 (12)	4788 (19)	1476 (31)
NA C(4)	4542 (9)	5570 (17)	2725 (23)
NA C(5)	3929 (16)	7366 (26)	3639 (30)
NA C(6)	3439 (12)	8404 (15)	3516 (26)
NA C(7)	2927 (10)	8041 (13)	2409 (28)
NA C(8)	2822 (9)	7194 (15)	1225 (20)
NA C(9)	3441 (8)	6370 (7)	1557 (19)
NA C(10)	3933 (7)	6582 (17)	2759 (25)
NA N	4501 (13)	7099 (21)	4565 (26)

satisfactorily accounted for; neither of the two ring H atoms of the picrate ion was visible. Another difference synthesis, calculated without any contribution from the 1-naphthylamine, is shown in Fig. 1 and suggests that there are at least two orientations of the 1-naphthyl-amine molecule. We have not succeeded in defining the location of the 1-naphthylamine in more detail.

We conclude that the C, N, O atoms of the pyridinium and picrate ions have been determined with reasonable precision and that the positions of the H atoms of pyridinium have been located approximately (but were not refined); the plane of the naphthylamine molecule has been determined but the orientations of the disordered naphthylamine molecules within this plane are known only roughly.

Atomic coordinates are given in Table 2.*

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* Lists of structure factors and anisotropic Debye–Waller factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35077 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
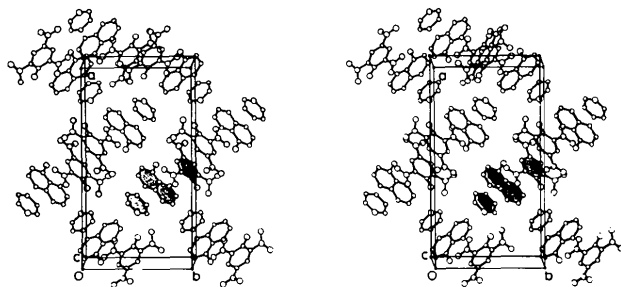
Results

(a) Crystal structure

The structure consists of centrosymmetric stacks of six moieties, with their planes approximately parallel: $(PY)^+(NA)(PC)^-\bar{1}(PC)^-(NA)(PY)^+$. The overall arrangement of these moieties is shown in Fig. 2 (stereoview) and in projection on to (001) (Fig. 3). The interplanar distances and angles in a grouping of six moieties are given in Table 3 and the equations of various planes in Table 4. Overlap diagrams corresponding to the pairs of moieties listed in Table 3 are shown in Figs. 4 and 5.

The intermolecular distances (Table 5) all indicate van der Waals interactions except for the distances between pyridinium N and phenolic and nitro O atoms of a picrate ion, which are 2·69 and 2·81 Å respectively. An N—H···O hydrogen bond to the phenolic O is clearly indicated, while the second contact may be either part of a bifurcated hydrogen bond or just a van der Waals contact. The position of the H atom attached to N is not known accurately enough for these possibilities to be distinguished.

Fig. 2. *ORTEP* stereoview (Johnson, 1965) of overall structure. For clarity only one orientation of 1-naphthylamine has been included (see Fig. 1 for details). Reference molecules (Table 2) are marked.
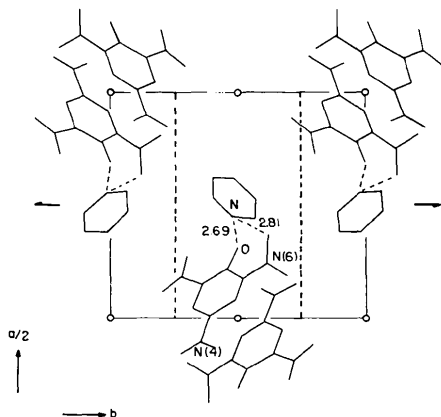

Fig. 3. Projection of part of the unit-cell contents on to (001), showing only the pyridinium and picrate moieties. The hydrogen bonds (Å) between the pyridinium in one grouping and the picrate in another are shown.

Table 3. *Interplanar distances and angles for the moieties in a grouping* $(PY)^+(NA)(PC)^-\bar{1}(PC)^-(NA)(PY)^+$

Pair of moieties	Distance (Å)	Angle (°)
Two picrates, related by $\bar{1}$	3·45 (1)	Necessarily parallel
Picrate–1-naphthylamine	3·38*	2·2
1-Naphthylamine–pyridinium	3·55*	4·8

* Errors not quoted because planes are not parallel.

Table 4. *Mean planes*

Equations of planes are expressed in the form $AX + BY + CZ + D = 0$ where X, Y, Z are coordinates in Å with respect to orthogonal axes and D is the origin to plane distance in Å. The transformation matrix is

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

|	A	B	C	D
(1) Plane through C(2)–C(6) of picrate	0·5784	0·5621	−0·5912	−10·8377
(2) Plane through NO₂ attached to C(2)	0·0723	−0·4317	0·8991	3·4242
(3) Plane through NO₂ attached to C(4)	0·5762	0·5744	−0·5814	−10·9587
(4) Plane through NO₂ attached to C(6)	0·5368	−0·5438	−0·6451	−10·3478
(5) Plane through atoms of pyridinium ring	0·6155	0·5466	−0·5677	−4·3287
(6) Plane through atoms of disordered 1-naphthylamine (coordinates in Table 2)	0·5476	0·5762	−0·6067	−7·3170
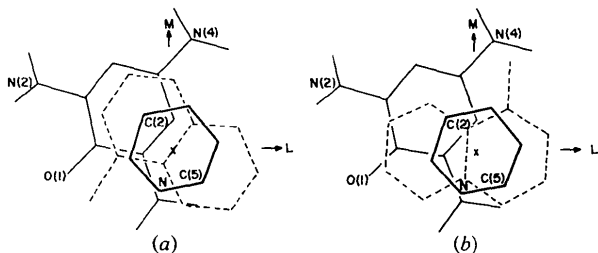
Fig. 4. Overlap diagram for the three moieties in a reference unit, projected on to the mean plane of the pyridinium ring; two possible orientations of 1-naphthylamine (see Fig. 1) are shown in (a) (full-line orientation) and (b) (broken-line orientation).
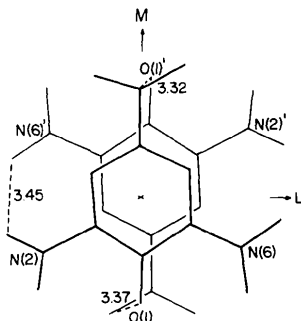

Fig. 6. Bond lengths (Å) and angles (°) of the pyridinium cation (mean e.s.d.'s are 0·009 Å and 0·6° respectively); the largest deviation from the best plane is 0·007 Å. The thermal ellipsoids are shown at the 50% probability level.

Fig. 5. Overlap diagram of two picrate ions related by a centre of symmetry.

Table 5. *Intermolecular distances* (Å) *for the ternary compound* ($\sigma \simeq 0.01$ Å)

Only distances <3·5 Å are given. Distances which involve 1-naphthylamine are not given because of the disordered arrangement of this component.

(a) Picric acid–picric acid (across a centre of symmetry) within a group

PC N(4)–PC O(1ᴵᴵ)	3·32	PC O(22)–PC O(61ᴵᴵ)	3·45
PC O(1)–PC O(42ᴵᴵ)	3·37	PC C(3)–PC O(6ᴵᴵ)	3·48
PC C(1)–PC C(4ᴵᴵ)	3·44		

(b) Picric acid–picric acid, between groups

PC O(22)–PC O(41ᴵᴵᴵ)	3·21	PC O(21)–PC O(41ᴵᴵᴵ)	3·39
PC N(2)–PC O(41ᴵᴵᴵ)	3·22		

(c) Picric acid–pyridine, between groups

PC O(1)–PY N(1ᴵⱽ)	2·69	PC O(22)–PY C(4ⱽᴵᴵ)	3·39
PC O(62)–PY N(1ᴵⱽ)	2·81	PC O(62)–PY C(ⱽᴵᴵᴵ)	3·44
PC O(62)–PY C(5ᴵⱽ)	3·08	PC O(21)–PY C(2ᴵˣ)	3·45
PC O(41)–PY C(1ⱽ)	3·23	PC O(21)–PY C(5ⱽᴵᴵ)	3·46
PC O(42)–PY C(4ⱽᴵ)	3·32	PC O(1)–PY C(1ᴵⱽ)	3·48

Symmetry code

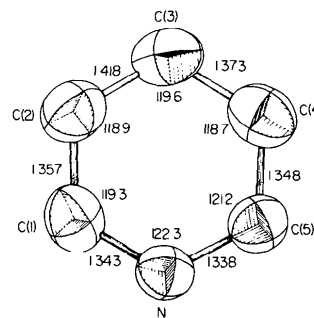|			
(I)	x, y, z	(VI)	$1 - x, 1 - y, 1 - z$
(II)	$1 - x, 2 - y, \bar{z}$	(VII)	$x, 1 + y, z$
(III)	$1 - x, 2 - y, 1 - z$	(VIII)	$x, y, z - 1$
(IV)	$\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$	(IX)	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$
(V)	$\frac{1}{2} + x, 1\frac{1}{2} - y, \bar{z}$		

(b) Pyridinium cation

The dimensions (Fig. 6) agree reasonably well with those found in pyridinium nitrate (Serewicz, Robertson & Meyers, 1965). Accurate dimensions have been determined by microwave spectroscopy for pyridine in the gas phase (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958); the less accurate values available for pyridinium do not differ significantly.

(c) Picrate anion

The dimensions (Fig. 7) agree reasonably well with those found in succinylcholine picrate (Jensen, 1975a) and carbamoylcholine picrate–picric acid (Jensen, 1975b), which, in turn, agree with earlier results. In particular we note that there are dimensional differences between the picrate ion and the picric acid molecule, which are most marked in the region of the phenolic O [e.g. C—OH $= 1.327$ (3) (Herbstein & Kaftory, 1976), 1.321 (4) (Jensen, 1975b); C—O⁻ $= 1.234$ (5) (Jensen, 1975a), 1.237 (4) Å (Jensen, 1975b)]. Five C atoms [C(2)–C(6)] are nearly coplanar but C(1) and O(1) are bent out of this plane; similar effects have been reported by Jensen and should presumably be ascribed to packing influences because the deviations from planarity are different in the several structures studied. The torsion angles of the nitro groups follow a familiar pattern, a fairly large torsion angle for one nitro group adjacent to the phenolic O, and small angles for the other two; the nitro group at C(6) is also bent up out of the mean plane.

No dimensions were obtained for the 1-naphthylamine molecule because of the disorder. The coordinates of Table 2 correspond to a rather distorted molecule, which is an artifact of the refinement process.

(d) The evidence for proton transfer

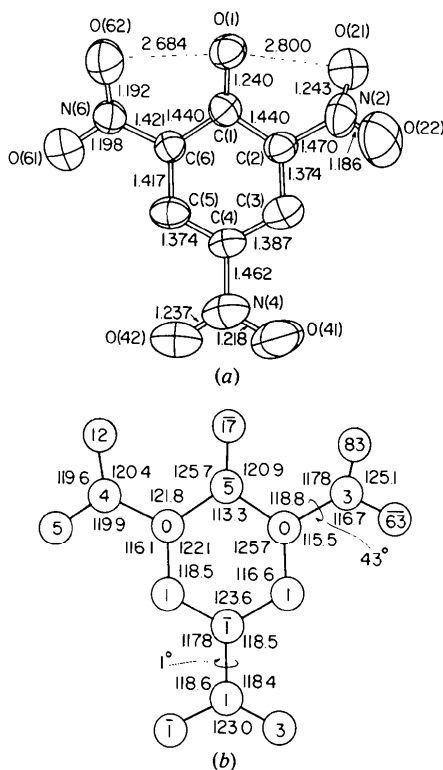An H atom attached to N was found in the difference synthesis in the plane of the pyridine ring; no

Fig. 7. Picrate ion : (a) atom nomenclature and bond lengths (Å) (σ ~ 0·009 Å); the thermal ellipsoids are shown at the 50% probability level; (b) bond angles (°) (σ ~ 0·6°), torsion angles (°) (σ ~ 0·6°) and deviations (units of 10^{-2} Å) from the plane of C(2)–C(6) (σ ~ 0·006 Å).

H attached to phenolic O was found in the difference synthesis for the picrate ion, but the weight of this result is somewhat reduced by our failure to find the H atoms attached to C(3) and C(5) in the same map. However, the evidence from the moiety dimensions, and in particular the value of C–O, 1·24 Å, is such that there seems to be little doubt about the ionic nature of the pyridinium and picrate moieties. The crystallographic evidence thus supports the conclusions drawn by Matsunaga & Saito (1972) from their IR studies.

Discussion

The pK_a values for the three components are: pyridine 5·23, 1-naphthylamine 3·92, picric acid 0·38. Thus, ionization of pyridine and picric acid ($\Delta pK_a = 4·85$) in the ternary complex is in accord with the rule of Johnson & Rumon (1965), which states that salts are formed when $\Delta pK_a > 3·8$ and molecular complexes when $\Delta pK_a < 3·8$. The occurrence of proton transfer in pyridinium picrate fits the rule. The situation in 1-naphthylamine–picric acid is not clear; the ΔpK_a

value (3·54) is near the border region but would appear to favour molecular-compound formation, with which the cell dimensions are compatible. On the other hand, the spectroscopic evidence (Matsunaga & Saito, 1972; Issa & El-Essawey, 1973) definitely points to salt formation.

The overall crystal structure can be described as a herring-bone arrangement of groups of six moieties stacked with parallel planes. The intrastack interactions are: (i) Charge-transfer interactions between 1-naphthylamine as donor and picrate ion as acceptor [picrate ion is about as strong an electron acceptor as picric acid (Saito & Matsunaga, 1972, 1973; Matsunaga & Saito, 1972)]. These authors have cited evidence for such charge-transfer interactions from a comparison of the electronic spectra of the ternary complex and those of binary molecular compounds of the components, taken pair-wise. (ii) Dipole–dipole interactions between the antiparallel picrate ions related by centres of symmetry (this arrangement also sets a maximal distance between negatively charged phenolic O atoms). In pyridinium picrate the stacked picrate ions are translationally equivalent and hence parallel, while the antiparallel ions in succinylcholine picrate are considerably more mutually offset than those in the present structure. (iii) Van der Waals interactions between pyridinium and 1-naphthylamine.

The principal interstack interactions are the hydrogen bonds between pyridinium N—H and picrate O⁻. The acceptor region presents a possibility of bifurcation of the hydrogen bond with one of the O atoms involved; in pyridinium picrate there is an analogous (possibly bifurcated) hydrogen bond, but there the roles of nitro and phenolic O atoms appear to be interchanged.

The packing arrangement found here is unusual but not unique. In the paramagnetic decamethylferrocenium–TCNQ dimer salt ([Fe{C$_5$(CH$_3$)$_5$}$_2$]$^{+\cdot}$)$_2$.- [TCNQ]$_2^{2-}$ (Reis, Preston, Williams, Peterson, Candela, Swartzendruber & Miller, 1979), the moieties are grouped into stacks of four units each: |DMFc]$^{+\cdot}$- [TCNQ]⁻[TCNQ]⁻[DMFc]$^{+\cdot}$. These finite stacks are arranged in a herring-bone fashion, adjacent stacks being approximately mutually perpendicular. Again, the infinite stacks that might have been expected were not found.

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