structure, the five-membered ring is more planar than that found in the related structures of Asu-containing peptides (Capasso, Mattia, Mazzarella & Zagari 1984*a,b*; Capasso, Mazzarella, Sica & Zagari, 1984), where, at least in one case, the maximum deviation from planarity is as high as 0·131 Å. The puckering of the ring, although generally small, significantly affects the dihedral angle ψ_1 about the C^α—C bond, whose value, in all the structures quoted, spans a range of almost 25°.

Inspection of the values of dihedral angles φ_1, ψ_1, φ_2 and ψ_2 in Table 3 clearly indicates that the overall conformation of the two molecules is of the type II′ β-bend, with the L-Asu residue in the second position and the Gly residue in the third position of the turn. This conformation, normally allowed for linear peptides with a D residue in the second position, is stabilized in aminosuccinyl peptides by the five-membered ring, which requires the value of ψ_1 to be close to $-120°$ and was predicted by us, on theoretical grounds, to be very stable for an L-Asu-Gly sequence. In addition, our solution studies on Boc-protected L-Asu-containing peptides show that, in non-H-acceptor solvents, this conformation is indeed the most stable one (manuscript in preparation). The II′ β-bend conformation, also adopted by Boc-L-Asu-L-Ala-Gly-OMe in the solid state (Capasso, Mazzarella, Sica & Zagari, 1984), is stabilized by an intramolecular 4→1 hydrogen bond between the N(3)H group of the L-Ala residue (position 4) and the carbonyl O(4) atom of the Boc group (position 1) [N(3)···O(4) 3·083 (3); N(3′)···O(4′) 2·945 (3) Å].

The folded conformation leaves only one of the two potential donor NH groups per molecule free to form intermolecular hydrogen bonds. The urethane NH group is hydrogen bonded to the carbonyl O(2′) atom, whereas the N′H group is hydrogen bonded to the ester O(6) atom of a screw-related unprimed unit [N(1)···O(2′) 2·998 (3); N(1′)···O(6) 2·918 (3) Å]. Thus, primed and unprimed units form chains of hydrogen-bonded molecules, which wind around the screw axes parallel to **a** (Fig. 2).

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Low-Temperature Structure of *N*-Methylphthalazinium Bis(7,7,8,8-tetracyano-*p*-quinodimethanide)

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Abstract. $(C_9H_9N_2)^+.(C_{12}H_4N_4)_2^-$, $M_r = 553·6$, monoclinic, $C2/c$, $a = 28·574\ (12)$, $b = 3·770\ (2)$, $c = 26·183\ (10)$ Å, $\beta = 114·29\ (3)°$, $V = 2570·85$ Å^3, $Z = 4$, $D_m = 1·38$ (measured by flotation in a mixture of chlorobenzene and bromobenzene), $D_x = 1·43$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 0·85$ cm^{-1}, $F(000) = 1140$, $T = 130$ K, $R = 0·0343$ for the 1097 reflections used in the rigid-body refinement. The structure consists of separate columns of TCNQ (7,7,8,8-tetracyano-*p*-quinodimethanide) and MPht (*N*-methylphthalazinium), oriented parallel to the *b* axis, each MPht being surrounded by six TCNQ molecules. At 130 K, the average spacings between the TCNQ and MPht molecules in the columns are 3·178 (2) and 3·449 (2) Å, respectively. The average net charge on the TCNQ molecules is estimated to be −0·38 to −0·44 units. The MPht molecules are disordered with two possible orientations of the methyl substituents.

Introduction. Structures of TCNQ salts which are quasi-one-dimensional conductors have been a subject of considerable interest in recent years. The structures

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of several TCNQ salts with nitrogen-containing heterocyclic cations have been determined (Fritchie, 1966; Kobayashi, Marumo & Saito, 1971; Kobayashi, 1974; Morosin, 1976). The title compound (for a drawing of the MPht cation see Fig. 1) was reported to be a new highly conducting salt by Rajchel, Przybylski, Graja, Pukacki, Wallwork & Willis (1983). The d.c. conductivity along the *b* axis of the crystal is 120 Ω^{-1} cm^{-1} at room temperature. The temperature dependence of the conductivity shows a 'metal-like' character above, and a semiconducting character below, 170 K.

This structure determination was undertaken as part of an investigation of structural aspects of Peierls transitions in organic crystals.

Experimental. MPhtI was prepared from commercial phthalazine and CH_3I (Gabriel & Miller, 1895). Its melting point is 508–511 K. The commercial TCNQ was purified by sublimation at 523 K. A single crystal of $MPht(TCNQ)_2$ was grown by slow diffusion across a fritted disk of solutions of MPhtI and TCNQ in acetonitrile, purified previously by stirring with silica gel and subsequent distillation over anhydrous P_2O_5. After one month, black plates with dimensions about 3 × 0·2 × 0·03 mm were found on both sides of the frit. The crystals do not melt below 573 K.

Low-temperature ($T = 130$ K) data were collected with graphite-monochromatized Mo $K\alpha$ radiation on a CAD-4 diffractometer equipped with a modified Nonius low-temperature apparatus. The crystal dimensions are 0·38 × 0·2 × 0·03 mm. From room-temperature Weissenberg photographs, the space group was determined to be either *C*2/*c* or *Cc*. Cell dimensions were determined from the setting angles of 25 reflections with $10 < \theta < 25°$. 4648 reflections with $\theta < 25°$ were measured by the $\omega/2\theta$ technique ($0 < h < 34$, $-4 < k < 4$, $-31 < l < 31$), and averaged to give 2640 unique reflections ($R_{\rm int} = 0{\cdot}029$). Five standard reflections, monitored throughout the data collection, showed no significant decrease in intensity. No absorption corrections were applied. Data were reduced with programs in the Enraf–Nonius (1979) *SDP* package. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The trial structure was obtained from isomorphous quinolinium–TCNQ (Kobayashi, Marumo & Saito, 1971). 1097 reflections with $F > 3\sigma(F)$ were used in the least-squares refinement. Since refinement in the non-centrosymmetric space group involves a large number of variables compared with the number of available observations, the program *LINEX*84 (Coppens, 1984) was used. It allows refinement of molecules as a rigid body, while retaining individual vibrational parameters. Weights used are defined by $w = 1/\sigma^2(F)$; $\sigma(F) = \sigma(F^2)^{1/2}/2F$; $\sigma(F^2) = [\sigma^2_{\rm counting} + (0{\cdot}02|F|^2)^2]^{1/2}$. Initial H-atom parameters were obtained with the program *HYDRA* (Enraf–Nonius, 1979). The MPht atomic parameters and the TCNQ rigid-body translational and rotational parameters were varied in every other cycle, while individual atomic parameters for TCNQ were adjusted in the alternate cycles. This procedure was followed for both the centrosymmetric and the non-symmetric treatment. In the latter, the TCNQ rigid-body and atomic parameters were constrained to retain the centrosymmetric relation between the two molecules. Without such constraint, convergence could not be achieved. The agreement factors obtained were for the centrosymmetric case: $R(F) = 0{\cdot}0343$, $wR(F) = 0{\cdot}0381$ with 82 parameters; and for the non-centrosymmetric case $R(F) = 0{\cdot}0338$, $wR(F) = 0{\cdot}0364$ and 139 parameters. The ratio of the *wR* factors (1·047) tests as just significant at the 0·005% confidence level ($R_{57,958,0.005} = 1{\cdot}044$), using the Hamilton (1965) test. Nevertheless, the non-centrosymmetric treatment gives non-positive-definite thermal parameters for four C and N and two H atoms of the phthalazinium ion. The effect is particularly pronounced for the H atom opposite the methyl group (*i.e.* at the $\bar{1}$-related position). It has a *U* value of $-0{\cdot}068$ Å^2 while the methyl carbon has unusually large thermal parameters, thus producing a pseudo-centrosymmetric arrangement. Since the parameters of the non-centrosymmetric model are not physically meaningful, the centrosymmetric space group is the preferred choice.

Final atomic coordinates and thermal parameters of the centrosymmetric treatment are listed in Table 1. Final shifts were smaller than $0{\cdot}1\sigma$. Bond lengths and angles are given in Table 2. Molecular diagrams indicating the atomic numbering scheme are shown in Fig. 2. A packing diagram is given in Fig. 3.*

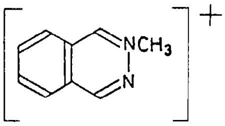

Fig. 1. The *N*-methylphthalazinium ion.

Discussion. There are five chemically different C—C bonds in TCNQ labelled *a* (C5—C6), *b* (C4—C5), *c* (C4—C8), *d* (C8—C11). Empirical relations between net charge and the bond length are

$$\text{charge} = 22{\cdot}43 - 23{\cdot}81\,(a+c)/(b+d) \qquad (1)$$

(Coppens & Guru Row, 1978), and

$$\text{charge} = 7{\cdot}25\,(b-c) - 8{\cdot}07\,(c-d) - 1 \qquad (2)$$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43955 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso}
MPht molecule*				
C1′	0·2664 (1)	0·2079 (9)	0·0757 (2)	3·3 (1)
C2′	0·3124 (1)	0·4433 (9)	0·0072 (2)	2·9 (1)
C3′	0·2382 (1)	0·1889 (10)	0·0173 (2)	3·1 (1)
C4′	0·3366 (2)	0·393 (2)	0·1474 (3)	1·7 (2)
CN1	0·3375 (1)	0·4616 (9)	0·0620 (2)	3·4 (1)
CN2	0·3132 (1)	0·3444 (8)	0·0952 (2)	3·6 (1)
H1′	0·252 (1)	0·15 (1)	0·104 (1)	5·1 (9)
H2′	0·3311 (1)	0·527 (8)	−0·014 (1)	2·7 (6)
H4′*A*	0·359 (2)	0·48 (2)	0·153 (3)	2‡
H4′*B*	0·316 (2)	0·44 (2)	0·165 (2)	2‡
H4′*C*	0·352 (2)	0·20 (2)	0·156 (3)	2‡
HCN1	0·383 (2)	0·54 (2)	0·083 (2)	2 (1)†
TCNQ molecule				
C1	0·0230 (1)	0·8044 (9)	0·1328 (1)	1·26 (8)
C2	0·0422 (1)	0·9062 (9)	0·0919 (1)	1·40 (9)
C3	0·0857 (1)	1·0978 (9)	0·1068 (1)	1·30 (9)
C4	0·1147 (1)	1·2037 (9)	0·1637 (1)	1·27 (8)
C5	0·0954 (1)	1·1012 (9)	0·2041 (1)	1·36 (8)
C6	0·0517 (1)	0·9113 (9)	0·1894 (1)	1·43 (9)
C7	−0·0216 (1)	0·6016 (8)	0·1175 (1)	1·35 (8)
C8	0·1598 (1)	1·4016 (8)	0·1792 (1)	1·33 (8)
C9	−0·0509 (1)	0·4909 (9)	0·0609 (1)	1·47 (9)
C10	0·1778 (1)	1·5230 (9)	0·1388 (1)	1·43 (8)
C11	0·1903 (1)	1·493 (1)	0·2363 (1)	1·59 (9)
C12	−0·0413 (1)	0·4942 (9)	0·1573 (1)	1·37 (8)
N1	−0·0738 (1)	0·3957 (8)	0·0156 (1)	2·42 (8)
N2	0·19138 (9)	1·6312 (8)	0·1061 (1)	2·13 (8)
N3	0·2146 (1)	1·5648 (8)	0·2821 (1)	2·66 (8)
N4	−0·05753 (9)	0·4055 (8)	0·1888 (1)	2·19 (8)
H2	0·0234 (9)	0·827 (8)	0·054 (1)	1·7 (6)†
H3	0·0975 (9)	1·160 (7)	0·079 (1)	0·8 (6)†
H5	0·1142 (9)	1·183 (8)	0·243 (1)	0·8 (6)†
H6	0·0402 (9)	0·847 (8)	0·216 (1)	1·5 (6)†

* Average value of two molecular orientations.
† Atoms refined isotropically.
‡ Isotropic temperature factors kept fixed during refinement.

Table 2. *Bond lengths* (Å) *and angles* (°)

TCNQ molecule			
C1—C2	1·440 (5)	C1—C2—C3	121·0 (3)
C2—C3	1·350 (4)	C2—C3—C4	121·3 (3)
C3—C4	1·433 (4)	C3—C4—C5	117·3 (3)
C4—C5	1·433 (5)	C4—C5—C6	121·6 (3)
C5—C6	1·351 (4)	C5—C6—C1	120·9 (3)
C6—C1	1·425 (4)	C6—C1—C2	117·8 (3)
C1—C7	1·396 (4)	C2—C1—C7	120·9 (2)
C4—C8	1·397 (4)	C6—C1—C7	121·3 (3)
C7—C9	1·433 (4)	C3—C4—C8	121·5 (3)
C7—C12	1·431 (5)	C5—C4—C8	121·2 (3)
C8—C10	1·429 (4)	C1—C7—C9	122·2 (3)
C8—C11	1·429 (4)	C1—C7—C12	122·2 (2)
C9—N1	1·153 (4)	C9—C7—C12	115·8 (3)
C12—N4	1·150 (5)	C4—C8—C10	121·6 (2)
C10—N2	1·150 (5)	C4—C8—C11	121·8 (3)
C11—N3	1·143 (4)	C10—C8—C11	116·6 (3)
		C7—C9—N1	178·6 (3)
		C7—C12—N4	179·2 (3)
		C8—C10—N2	177·7 (4)
		C8—C11—N3	179·6 (4)
MPht molecule*			
C1′—CN2	1·324 (5)	CN2—CN1—C2′	118·4 (3)
CN2—CN1	1·388 (6)	CN1—C2′—C3′	120·8 (3)
CN1—C2′	1·318 (5)	C2′—C3′—C3′	119·8 (3)
C2′—C3′	1·410 (5)	C3′—C3′—C1′	117·8 (3)
C3′—C3′	1·413 (7)	C3′—C1′—CN2	118·5 (4)
C3′—C1′	1·406 (5)	C1′—CN2—CN1	124·7 (4)
CN2—C4′	1·262 (7)	C1′—CN2—C4′	118·4 (5)
		CN1—CN2—C4′	116·8 (4)
		C2′—C3′—C1′	122·4 (4)

* Average value of two molecular orientations.

(Flandrois & Chasseau, 1977). The values obtained with these equations (Table 3) are slightly lower than the stoichiometric average charge of −0·5. They should be compared with the value of −0·5 derived from diffuse-scattering measurements for quinolinium-$(TCNQ)_2$ (Pouget, 1981).

The angle between the *b* axis and the TCNQ molecular normals is 32·5 (1)°. The intermolecular spacing of the TCNQ molecules is 3·178 (2) Å, somewhat shorter than the room-temperature values of 3·22 Å in quinolinium$(TCNQ)_2$ (Kobayashi, Marumo & Saito, 1971) and 3·246 Å in acridinium$(TCNQ)_2$ (Kobayashi, 1974), and longer than the 100 K value of 3·113 (1) Å for TTF–TCNQ (Schultz, Stucky, Blessing & Coppens, 1976). The spacing of the MPht molecules is 3·449 (2) Å, while the angle between the *b* axis and the normal to the MPht molecule is 23·83 (9)°.

The MPht cations have two equally populated orientations in the centrosymmetric model. The elongation of the 'thermal ellipsoids' in the direction of the long molecular axis indicates that the two orientations do not exactly overlap. Therefore the parameters and molecular dimensions in Tables 1 and 2 must be considered averages over the two molecular orientations only.

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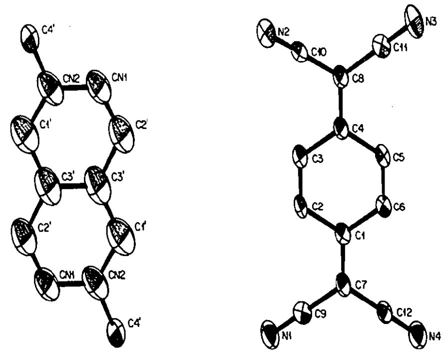

Fig. 2. Molecular diagrams showing labelling of atoms. Ellipsoids are 50% probability surfaces.

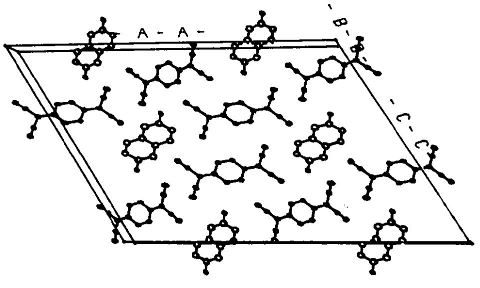

Fig. 3. Packing diagram.

Table 3. *Net molecular charge on TCNQ*

Bonds*	*a*	*b*	*c*	*d*
Length (Å)	1·351	1·433	1·397	1·431
From (1)	$(a+c)/(b+d)=0\cdot959$;charge = −0·40			
From (2)	$b-c=0\cdot036$ Å;	$c-d=-0\cdot034$ Å; charge = −0·46		

* *a*: Average of C2—C3, C5—C6; *b*: average of C1—C2, C1—C6, C3—C4 and C4—C5; *c*: average of C1—C7, C4—C8; *d*: average of C7—C9, C7—C12, C8—C10 and C8—C11.

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Structure of 1-Methyl-3-(2-methyl-2-nitrovinyl)indole

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Abstract. $C_{12}H_{12}N_2O_2$, $M_r = 216\cdot24$, orthorhombic, *Fdd*2, $a = 24\cdot398$ (1), $b = 24\cdot914$ (1), $c = 7\cdot202$ (1) Å, $V = 4378\cdot1$ (2) Å^3, $Z = 16$, $D_x = 1\cdot312$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0\cdot852$ cm^{-1}, $F(000) = 1824$, room temperature, $R = 0\cdot056$ for 1156 observed reflections [$I > 3\sigma(I)$]. The study of bond distances and torsion angles in both the indole ring and the nitrovinyl side chain shows that the electronic structure of the molecule can be described in terms of a number of resonance structures according to the valence-bond theory. The molecules are packed in pairs and, in these pairs, the distances between the overlapping zones indicate a charge-transfer interaction.

Introduction. A series of 3-(2-nitrovinyl)indoles have been prepared as potential antiparasite drugs. The title compound exhibits a considerable antiparasitic activity against *Candida albicans*. Many of the common drugs of clinical use consist of two parts: a heterocyclic system and an ionophoric one connected through an ethylene bridge (Rodriguez, Subirats & Canoira, unpublished results). In the present compound an indole ring and a nitro group are separated by the ethylene bridge. The molecular and crystallographic analysis of this compound could be interesting to help understand the possible parameters responsible for the activity.

Experimental. Synthetized, in good yield, by condensation of 3-formyl-1-methylindole with excess nitromethane (Ash & Wragg, 1958). Crystals obtained by slow evaporation of an ethanolic solution; transparent, orange-yellow, metallic bright, needle-shaped crystals, m.p. 400–402 K. Enraf–Nonius CAD-4 diffractometer. Crystal size 0·6 × 0·15 × 0·21 mm. Cell dimensions from setting angles of 62 reflections ($10 < 2\theta < 88°$). Graphite-monochromated Mo $K\alpha$ radiation; no absorption correction. 1780 reflections, $\omega/2\theta$ scan technique, $\theta_{\max} = 30°$, 1156 considered observed with $I > 3\sigma(I)$, index range: h 0 to 34, k 0 to 34, l 0 to 10. Two standard reflections, monitored every 90 min, showed no significant variation in intensity. Structure solved by direct methods, *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); 15 non-H atoms found in the first E map; missing C(13) located on a difference Fourier map. Least-squares refinement of non-H atoms with isotropic temperature factors; final refinement (on F, 144 parameters) was of non-H atoms with anisotropic temperature factors adding H atoms in calculated positions with isotropic temperature factors. $R = 0\cdot056$, $wR = 0\cdot058$, $S = 0\cdot89$, weighting scheme of Martínez-Ripoll & Cano (1975). $(\Delta/\sigma)_{\max} = 0\cdot04$; Max., min. $\Delta\rho = 0\cdot24$, $-0\cdot29$ e Å^{-3}. Atomic scattering factors from

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