Table 3. *Net molecular charge on TCNQ*

Bonds*	*a*	*b*	*c*	*d*
Length (Å)	1·351	1·433	1·397	1·431
From (1)	$(a+c)/(b+d)=0·959$;charge = −0·40			
From (2)	$b-c=0·036$ Å;	$c-d=-0·034$ 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. $C_{12}H_{12}N_2O_2$, $M_r = 216·24$, orthorhombic, *Fdd*2, $a = 24·398$ (1), $b = 24·914$ (1), $c = 7·202$ (1) Å, $V = 4378·1$ (2) Å^3, $Z = 16$, $D_x = 1·312$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·852$ cm^{-1}, $F(000) = 1824$, room temperature, $R = 0·056$ 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parts: a heterocyclic system and an ionophoric one connected through an ethylene bridge (Rodriguez, Subirats & Canoira, unpublished results).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. $R = 0·056$, $wR = 0·058$, $S = 0·89$, weighting scheme of Martínez-Ripoll & Cano (1975). $(\Delta/\sigma)_{\max} = 0·04$; Max., min. $\Delta\rho = 0·24$, $-0·29$ e Å^{-3}. Atomic scattering factors from

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International Tables for X-ray Crystallography (1974). Computations carried out on a VAX 11/750 computer using *XRAY70* (Stewart, Kundell & Baldwin, 1970) and *PARST* (Nardelli, 1983).

Discussion. Final atomic parameters and equivalent isotropic *U*'s are listed in Table 1,* interatomic distances and angles in Table 2. Fig. 1 shows a view of the molecule with the numbering scheme. Bond distances and angles have the expected values, C(3)—C(4) = 1·358 (6) Å being shorter. The pyrrole ring is planar within the error limits with C(2) showing the maximum deviation from the mean plane. The bond distances in the five-membered ring and the planarity of the sequence C(2)—N(1)—C(9)—C(8), torsion angle −0·9 (5)°, indicate a delocalization of the charge at N(1). The indole nucleus is planar with a maximum deviation of −0·022 (5) Å at C(8). The torsion angles* indicate that the nitrovinyl group is almost planar [maximum deviation from the plane through C(8)—C(10)—C(11)—N(2) −0·011 (5) Å at C(10)]; the O atoms O(21) and O(22) are out of this plane by −0·099 (7) and 0·136 (7) Å, respectively, and the plane is twisted by 20·0 (4)° with respect to the plane of the indole nucleus. We think that high values of this twist angle can prevent molecular conjugation and hence could be a molecular parameter responsible for the activity of the (nitrovinyl)indoles. The N(2)—O(21) = 1·219 (5) and N(2)—O(22) = 1·224 (5) Å bond distances have intermediate single-bond–double-bond character; N(2)—C(11) and C(11)—C(12) are slightly shorter while C(10)—C(11) is slightly longer than the respective expected values. The shortening of the C(8)—C(10) bond is remarkable. According to these bond distances the molecule can be considered as a resonance hybrid of the following structures:

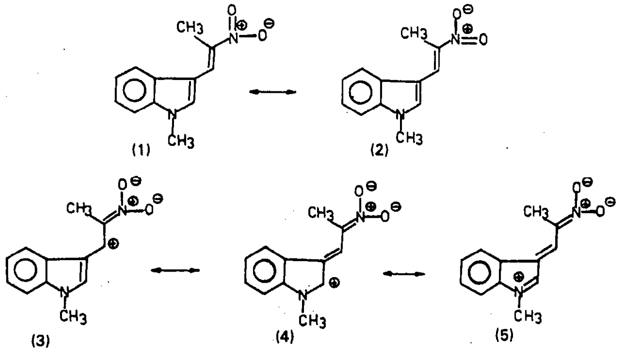

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(a_i,a_j).$$

	x	y	z	U_{eq}
N(1)	1·0261 (1)	0·3550 (1)	0·2866 (8)	47 (1)
C(2)	1·0758 (1)	0·3313 (1)	0·3248 (8)	40 (1)
C(3)	1·1281 (2)	0·3539 (2)	0·3451 (9)	53 (1)
C(4)	1·1705 (2)	0·3203 (2)	0·3829 (9)	59 (1)
C(5)	1·1628 (2)	0·2645 (2)	0·4003 (9)	55 (1)
C(6)	1·1112 (2)	0·2415 (2)	0·3814 (8)	44 (1)
C(7)	1·0671 (1)	0·2754 (1)	0·3424	37 (1)
C(8)	1·0088 (1)	0·2669 (1)	0·3172 (7)	37 (1)
C(9)	0·9864 (1)	0·3169 (1)	0·2837 (8)	43 (1)
C(10)	0·9838 (1)	0·2148 (1)	0·3170 (7)	41 (1)
C(11)	0·9300 (1)	0·2030 (1)	0·3374 (8)	39 (1)
C(12)	0·8839 (2)	0·2399 (2)	0·3781 (9)	54 (1)
C(13)	1·0181 (2)	0·4122 (2)	0·2504 (10)	65 (2)
N(2)	0·9158 (1)	0·1464 (1)	0·3261 (8)	53 (1)
O(21)	0·8685 (2)	0·1336 (2)	0·3591 (9)	78 (1)
O(22)	0·9503 (1)	0·1130 (1)	0·2837 (10)	82 (2)

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

N(1)—C(2)	1·375 (5)	C(7)—C(8)	1·449 (5)
N(1)—C(9)	1·358 (5)	C(8)—C(9)	1·382 (5)
N(1)—C(13)	1·463 (5)	C(8)—C(10)	1·433 (5)
C(2)—C(3)	1·401 (6)	C(10)—C(11)	1·353 (5)
C(2)—C(7)	1·414 (5)	C(11)—C(12)	1·483 (6)
C(3)—C(4)	1·358 (6)	C(11)—N(2)	1·454 (5)
C(4)—C(5)	1·409 (7)	N(2)—O(21)	1·219 (5)
C(5)—C(6)	1·390 (6)	N(2)—O(22)	1·224 (5)
C(6)—C(7)	1·396 (5)		
C(9)—N(1)—C(13)	125·7 (3)	C(2)—C(7)—C(8)	106·3 (2)
C(2)—N(1)—C(13)	124·9 (3)	C(7)—C(8)—C(10)	123·4 (3)
C(2)—N(1)—C(9)	109·4 (3)	C(7)—C(8)—C(9)	106·2 (3)
N(1)—C(2)—C(7)	107·9 (3)	C(9)—C(8)—C(10)	130·3 (3)
N(1)—C(2)—C(3)	130·6 (3)	N(1)—C(9)—C(8)	110·2 (3)
C(3)—C(2)—C(7)	121·5 (3)	C(8)—C(10)—C(11)	127·6 (3)
C(2)—C(3)—C(4)	117·9 (4)	C(10)—C(11)—N(2)	115·9 (3)
C(3)—C(4)—C(5)	121·6 (4)	C(10)—C(11)—C(12)	128·6 (3)
C(4)—C(5)—C(6)	121·2 (4)	C(12)—C(11)—N(2)	115·5 (3)
C(5)—C(6)—C(7)	118·0 (3)	C(11)—N(2)—O(22)	120·6 (3)
C(2)—C(7)—C(6)	119·8 (2)	C(11)—N(2)—O(21)	118·0 (3)
C(6)—C(7)—C(8)	133·9 (2)	O(21)—N(2)—O(22)	121·4 (4)

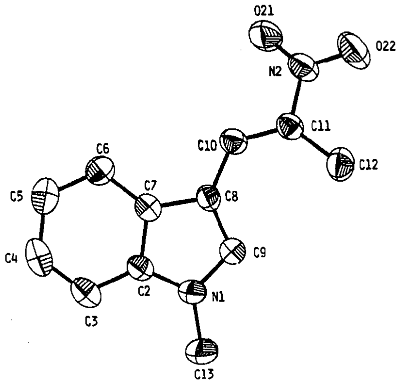

Fig. 1. *ORTEP* view (Johnson, 1976) of the molecules with the atomic numbering.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43904 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

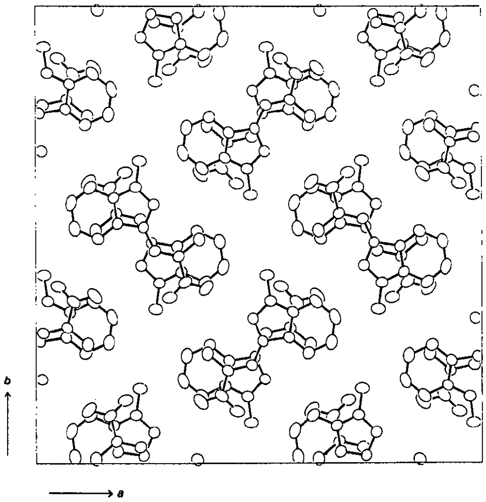

Fig. 2. Molecular packing viewed down the *xy* plane.

Although the torsion angle between the side chain and the indole nucleus reaches the value of 20·0 (4)°, the perturbation of the pyrrole ring by the polar effect of the nitro group seems to be important because the contribution of the resonance structures (4) and (5) agrees well with the observed bond lengths. Moreover, it has been suggested (Bücki & Mak, 1977) that the contribution of the resonance structure (5) is important in the resonance hybrid, since the IR absorption of the 3-(2-nitrovinyl)indoles shows several stretching C=C and C=N bands, while the polar effect of the nitro group is evidenced by the bathochromic effect of both stretching bands of this group about 1300 and 1250 cm^{-1}.

The deviations in the side-chain and pyrrole-ring bond distances from the normal values can be explained by taking into account the molecular packing, Fig. 2. The molecules stack up along the *c* axis forming dimers through a charge-transfer interaction between the nitrovinyl chain (acceptor) and the indole nucleus (donor), molecular zones which are parallel in the dimer (Fig. 2). The molecular overlapping in these zones gives an interplanar distance of 3·50 Å which corresponds to the values usually found for this type of charge-transfer interaction (Foster, 1973).

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Biphenyl-2,2′-dicarboxylic Acid (Diphenic Acid)

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Abstract. $C_{14}H_{10}O_4$, $M_r = 242{\cdot}2$, monoclinic, $P2_1/c$, $a = 14{\cdot}032\,(3)$, $b = 11{\cdot}952\,(3)$, $c = 13{\cdot}616\,(3)$ Å, $\beta = 91{\cdot}46\,(2)°$, $V = 2282{\cdot}8\,(16)$ Å^3, $Z = 8$, $D_x = 1{\cdot}410$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}97$ cm^{-1}, $F(000) = 1008$, $T = 296$ K, $R = 0{\cdot}064$ for 3366 observations (of 4008 unique data). The unit cell contains two independent molecules. The dihedral angles between the two ring planes are 71·3 (1)° in one molecule (*A*) and 83·6 (1)° in the other (*B*). In both molecules the carboxyl groups are located on opposite sides of the rings such that the C(2)—C(1)—C(1′)—C(2′) torsion angles are −119·3 (2)° in *A* and −106·3 (2)° in *B*.

Introduction. Interest in the interactions of neighboring groups on the orientation of carboxyl groups led us to examine the crystal structures of some *ortho*-substituted benzoic acids (Chiari, Fronczek, Davis & Gandour,

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