

## The Crystal and Molecular Structure of 3-(*N*-Phenyl-*N*-tricyanovinyl)amino-1,2,5-triphenylpyrrole

BY JOHN J. STEZOWSKI

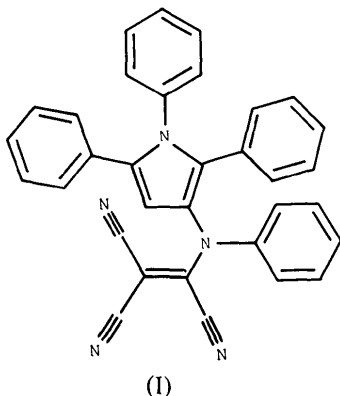
Institut für Organische Chemie, Biochemie und Isotopenforschung der Universität Stuttgart, Pfaffenwaldring 55, 7000 Stuttgart 80, Federal Republic of Germany

(Received 5 January 1977; accepted 5 February 1977)

$C_{33}H_{21}N_5$  is monoclinic, space group  $C2/c$ , with (at  $ca -150^\circ C$ )  $a = 35.969(7)$ ,  $b = 9.161(1)$ ,  $c = 17.328(3)$  Å,  $\beta = 113.68(1)^\circ$ ,  $Z = 8$ . Intensities were measured with monochromated Mo  $K\alpha$  ( $\lambda = 0.71069$  Å) radiation, with a crystal cooled to  $ca -150^\circ C$ , to a resolution of  $\sin \theta/\lambda < 0.816$  Å $^{-1}$ . Block-diagonal least-squares refinement of 427 variables with 8374 reflexions resulted in  $R = 0.078$  and  $R_w = 0.083$ . The interactions between the pyrrole moiety and its substituents have been found to be inductive in nature. The implications of the effects of electron donation from the pyrrole *N*-phenyl substituent to the pseudo-aromatic heterocyclic ring on the lengths of the  $C_\alpha-N$  bonds are examined. There is evidence of extensive conjugation within the 3-(*N*-phenyl-*N*-tricyanovinyl)amino moiety (an *N,N*-disubstituted anilinc in which one of the substituents is a strongly electron-withdrawing tricyanovinyl group).

### Introduction

The title compound (I) contains three functional groups: a highly substituted pyrrole moiety, and an *N*-substituted aniline moiety which serves as a bridging group between the pyrrole ring and the third functional group which is a tricyanovinyl moiety. This report details the crystal-structure analysis and presents an examination of the bonding geometry in an effort to clarify the interactions between the substituents.



### Experimental

The title compound crystallizes in  $C2/c$  with one molecule per asymmetric unit. The lattice parameters ( $ca -150^\circ C$ ), obtained by least squares (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) from automatically centred  $2\theta$  values for 75 reflexions in the angular range  $30.4 < 2\theta < 44.6^\circ$  (Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å, monochromatized), are:  $a = 35.969(7)$ ,  $b = 9.161(1)$ ,  $c = 17.328(3)$  Å,  $\beta = 113.68(1)^\circ$ ;  $D_x = 1.238$  g  $cm^{-3}$ .

A transparent, red,  $0.25 \times 0.40 \times 0.42$  mm parallelepiped, cut from an elongated platelet and enclosed in a thin-walled glass capillary, was used for all crystallographic measurements. The crystal was maintained at  $ca -150^\circ C$  (Syntex LT-1 low-temperature device) for the measurement of intensities with a Syntex  $P\bar{1}$  autodiffractometer operating in an  $\omega$ -scan mode. The scan range was  $0.75^\circ$ ; the scan rate was allowed to vary from  $2.0$  to  $24.0^\circ \text{ min}^{-1}$  as a function of the maximum peak intensity; and background was measured on each side of the reflexion ( $\Delta\omega = 1.0^\circ$  from the reflexion centre) for half the total scan time. Three reference reflexions, measured periodically, remained constant to within 3.3% of their initial intensities. Of the 11 262 unique reflexions ( $\sin \theta/\lambda \leq 0.816$  Å $^{-1}$ ), 5958 were classified as observed [ $I \geq 2.0\sigma(I)$ ]. Lorentz and polarization corrections were applied; absorption corrections were not considered necessary.

### Structure determination and refinement

The structure was solved by direct methods;\* coordinates for the H atoms were obtained from difference maps. All atomic coordinates, anisotropic temperature factors for C and N atoms, isotropic temperature factors for H atoms and a single scale factor were refined by block-diagonal least squares. The blocks were constructed with the parameters associated with a C or N atom and any H atoms bonded to it. In addition to the data which had been classified as observed, those with  $I_c > 2\sigma(I)$  also contributed to the refinement. In this

\* Unless otherwise indicated, XRAY 72 (Stewart *et al.*, 1972) was used for all calculations.

Table 1. *R* as a function of  $\sin \theta$ 

$\sin \theta$	<i>R</i>	$\sin \theta$	<i>R</i>
0.10	0.031	0.40	0.063
0.20	0.050	0.50	0.112
0.30	0.054	0.60	0.161

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) for nitrogen and carbon atoms with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	1479 (1)	-40 (3)	3271 (1)
C(11)	1872 (1)	-8 (4)	3951 (2)
C(12)	2164 (1)	-996 (5)	3946 (3)
C(13)	2547 (1)	-973 (6)	4586 (3)
C(14)	2632 (1)	16 (7)	5245 (3)
C(15)	2340 (2)	1002 (6)	5264 (3)
C(16)	1952 (1)	1009 (5)	4594 (2)
C(2)	1352 (1)	950 (3)	2614 (2)
C(21)	1610 (1)	2145 (3)	2538 (2)
C(22)	1977 (1)	1870 (4)	2468 (2)
C(23)	2209 (1)	3011 (5)	2370 (3)
C(24)	2073 (1)	4438 (4)	2322 (2)
C(25)	1712 (1)	4725 (4)	2392 (3)
C(26)	1482 (1)	3590 (3)	2509 (2)
C(3)	975 (1)	500 (3)	2067 (2)
N(3)	738 (1)	1162 (3)	1266 (2)
C(31)	503 (1)	2459 (3)	1242 (2)
C(32)	589 (1)	3757 (4)	928 (2)
C(33)	370 (1)	5009 (4)	939 (2)
C(34)	71 (1)	4950 (5)	1248 (3)
C(35)	-18 (1)	3635 (5)	1538 (3)
C(36)	201 (1)	2378 (4)	1548 (2)
C(4)	866 (1)	-785 (3)	2381 (2)
C(5)	1184 (1)	-1102 (3)	3133 (2)
C(51)	1214 (1)	-2303 (3)	3716 (2)
C(52)	1041 (1)	-3656 (4)	3382 (2)
C(53)	1056 (1)	-4820 (4)	3904 (2)
C(54)	1244 (1)	-4671 (4)	4777 (3)
C(55)	1411 (1)	-3333 (4)	5119 (2)
C(56)	1398 (1)	-2163 (4)	4597 (2)
C(6)	724 (1)	539 (3)	551 (2)
C(61)	396 (1)	1037 (4)	-223 (2)
N(61)	131 (1)	1361 (4)	-832 (2)
C(7)	969 (1)	-549 (3)	467 (2)
C(71)	1313 (1)	-1156 (4)	1127 (2)
N(71)	1604 (1)	-1713 (4)	1598 (2)
C(72)	894 (1)	-1103 (4)	-352 (2)
N(72)	845 (1)	-1553 (3)	-1015 (2)

manner, 8374 empirically weighted data,  $\sigma^2(F) = \sigma_o^2(F) + 0.0125(F) + 0.0005(F)^2$ , contributed to the refinement of 427 variables to give  $R = 0.078$  and  $R_w = 0.083$ , and an estimated standard deviation of an observation of unit weight of 1.50. Examination of the data indicated the absence of significant extinction.

In view of the presence of the tricyanovinyl moiety and the high resolution of the data, additional refinement with a truncated data set to minimize the effects of the delocalized valence electrons (Lemley, Skarstad & Hughes, 1976) was considered. Unfortunately, the quality of the higher-angle data does not appear to

Table 3. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^2$ ) for hydrogen atoms

Hydrogen atom designations correspond to those of the atom to which they are bonded.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(12)	2107 (17)	-1721 (69)	3437 (36)	9.9
H(13)	2814 (20)	-1679 (75)	4387 (38)	13.7
H(14)	2898 (19)	-11 (70)	5762 (37)	11.1
H(15)	2343 (19)	1746 (71)	5865 (39)	11.2
H(16)	1733 (15)	1655 (56)	4655 (29)	6.3
H(22)	2070 (13)	859 (51)	2475 (26)	5.1
H(23)	2457 (15)	2766 (56)	2249 (28)	6.7
H(24)	2227 (16)	5240 (59)	2118 (32)	7.6
H(25)	1636 (14)	5682 (55)	2431 (27)	5.7
H(26)	1233 (12)	3810 (44)	2609 (23)	3.7
H(32)	799 (11)	3693 (39)	681 (21)	2.6
H(33)	443 (17)	5915 (67)	586 (36)	9.8
H(34)	-129 (15)	5815 (59)	1295 (29)	7.4
H(35)	-243 (13)	3538 (51)	1818 (27)	5.7
H(36)	141 (17)	1358 (63)	1928 (34)	9.7
H(4)	584 (17)	-1278 (64)	2318 (34)	8.6
H(52)	906 (11)	-3756 (42)	2818 (24)	3.2
H(53)	930 (13)	-5834 (52)	3635 (26)	5.0
H(54)	1296 (13)	-5525 (51)	5248 (27)	5.5
H(55)	1550 (10)	-3214 (40)	5732 (21)	2.3
H(56)	1513 (11)	-1200 (46)	4893 (24)	3.9

justify such a refinement. In particular, the distribution of *R* as a function of  $\sin \theta$  (Table 1), and the relatively high percentage of unobserved data in the truncated set that would contribute to the refinement (35% of the 5845 contributing reflexions) were taken as indications that the resultant refinement would not necessarily improve the accuracy of the model. Therefore, the possibility of further refinement was not pursued.

The resultant atomic coordinates from refinement with the full data set are presented in Tables 2 and 3.\*

## Discussion

Some insight into the interactions between the various components of (I) can be gained from an examination of the molecular conformation presented in Fig. 1. Clearly none of the pyrrole substituents display a coplanar orientation with the five-atom ring. In contrast, Fig. 1 reveals near coplanarity between the atoms bonded to N(3) and the tricyanovinyl moiety. These observations are confirmed by the dihedral angles (Table 4). Thus the geometry of the pyrrole moiety can be discussed separately from that of the aniline and tricyanovinyl moieties. Bond distances and angles are presented in Tables 5 and 6.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32496 (57 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

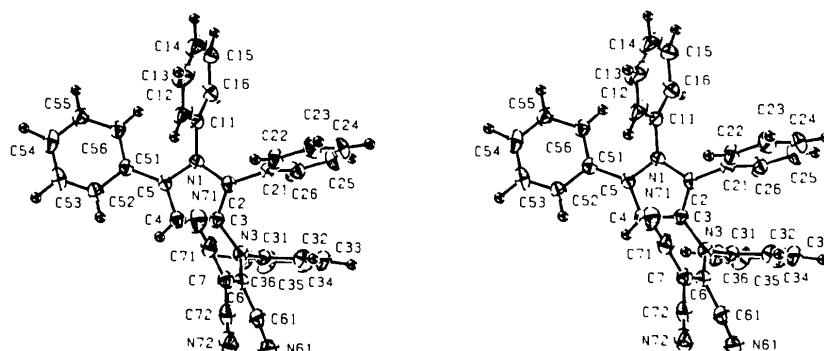


Fig. 1. Stereoscopic projection (Johnson, 1971) of 3-(*N*-phenyl-*N*-tricyanovinyl)amino-1,2,5-triphenylpyrrole. Carbon and nitrogen atoms are drawn with thermal ellipsoids representative of the 65% probability level for the refined thermal parameters. Hydrogen atoms are depicted with arbitrary isotropic temperature factors ( $B = 0.75 \text{ \AA}^2$ ).

Table 4. Selected dihedral angles ( $^\circ$ ) with estimated standard deviations in parentheses

C(2)N(1)C(11)C(12)	-102.4 (4)
C(3)C(2)C(21)C(22)	-113.0 (4)
C(4)C(3)N(3)C(6)	-73.9 (4)
C(4)C(5)C(51)C(52)	35.7 (5)
C(3)N(3)C(6)C(7)	-13.1 (5)
C(3)N(3)C(31)C(32)	118.1 (3)
C(6)C(6)C(7)C(71)	177.6 (3)
C(6)C(6)C(7)C(72)	0.7 (5)

Table 5. Bond distances ( $\text{\AA}$ ) between carbon and nitrogen atoms with estimated standard deviations in parentheses

N(1)-C(2)	1.383 (4)	C(11)-C(12)	1.388 (6)
N(1)-C(5)	1.388 (4)	C(11)-C(16)	1.390 (5)
C(2)-C(3)	1.369 (4)	C(12)-C(13)	1.379 (5)
C(4)-C(5)	1.376 (3)	C(13)-C(14)	1.391 (8)
C(3)-C(4)	1.417 (5)	C(14)-C(15)	1.398 (8)
N(1)-C(11)	1.432 (3)	C(15)-C(16)	1.411 (6)
C(2)-C(21)	1.475 (5)	C(21)-C(22)	1.396 (5)
C(3)-N(3)	1.438 (4)	C(21)-C(26)	1.396 (5)
C(5)-C(51)	1.468 (4)	C(22)-C(23)	1.389 (6)
N(3)-C(31)	1.449 (4)	C(23)-C(24)	1.386 (6)
N(3)-C(6)	1.347 (4)	C(24)-C(25)	1.375 (7)
C(6)-C(7)	1.376 (5)	C(25)-C(26)	1.394 (6)
C(6)-C(61)	1.459 (4)	C(31)-C(32)	1.392 (5)
C(7)-C(71)	1.418 (4)	C(31)-C(36)	1.391 (6)
C(7)-C(72)	1.428 (5)	C(32)-C(33)	1.395 (6)
C(61)-N(61)	1.141 (4)	C(33)-C(34)	1.383 (7)
C(71)-N(71)	1.156 (4)	C(34)-C(35)	1.391 (6)
C(72)-N(72)	1.165 (5)	C(35)-C(36)	1.391 (6)
		C(51)-C(52)	1.403 (4)
C(61)-N(61)	1.160*	C(51)-C(56)	1.404 (4)
C(71)-N(71)	1.169*	C(52)-C(53)	1.386 (5)
C(72)-N(72)	1.175*	C(53)-C(54)	1.393 (5)
		C(54)-C(55)	1.388 (5)
		C(55)-C(56)	1.391 (5)

\* Corrected for riding motion (Busing & Levy, 1964; Busing, Martin & Levy, 1964).

The pyrrole ring displays approximate  $C_{2v}$  symmetry. The appropriate bond distances, including those to the phenyl substituents at C(2) and C(5), are equivalent to within two estimated standard deviations. The most notable exceptions from ideal symmetry occur for the endocyclic angles about the  $C_\beta$  atoms, only one of which is substituted, and in the exocyclic angles about the  $C_\alpha$  atoms; the latter deviations may reflect the differing orientations of their respective phenyl substituents. The pyrrole bond distances are systematically longer than those reported for [*S*(*R,R*)]-viminol (Silverton & Lloyd, 1975) [hereafter *S*(*R,R*)-v]. The differences are small, less than or equal to 0.010  $\text{\AA}$ , but are very likely indicative of the diminished importance of the valence electrons (Lemley *et al.*, 1976) in the present refinement.

A systematic difference exists between the  $C_\alpha$ -N and  $C_\alpha$ - $C_\beta$  distances in (I) and *S*(*R,R*)-v, and those determined by microwave spectroscopy (Nygaard, Nielsen, Kirchheiner, Maltesen, Rastrup-Andersen & Sørensen, 1969). The microwave investigation produced  $C_\alpha$ -N distances 0.012  $\text{\AA}$  shorter than the  $C_\alpha$ - $C_\beta$  distances, whereas in the two crystal-structure analyses the reverse is true (Fig. 2). The pyrrole ring in the crystal-structure determinations contains both C and N substituents, while the microwave results are for the parent compound. Thus the substituent effects merit examination before an assessment of the significance of these differences can be attempted.

The nature of the substituents in the crystallographic studies differs in electronic character. In (I), all substituents are bonded to the pyrrole ring through  $sp^2$ -hybridized C or N atoms, whereas in *S*(*R,R*)-v they are bonded through  $sp^3$ -hybridized C atoms. Thus the pyrrole-substituent interactions in the latter can arise only from inductive effects, while (I) possesses the possibility of conjugative interaction. With respect to the latter possibility, attention has been called above to the fact that the various pyrrole substituents were not coplanar with the heterocyclic ring, and thus are not

Table 6. Bond angles ( $^{\circ}$ ) with estimated standard deviations in parentheses

C(2)N(1)C(5)	109.9 (2)	C(11)C(12)C(13)	119.9 (4)
C(2)N(1)C(11)	123.7 (3)	C(12)C(13)C(14)	119.4 (5)
C(5)N(1)C(11)	126.2 (2)	C(13)C(14)C(15)	121.3 (4)
N(1)C(2)C(3)	106.2 (2)	C(14)C(15)C(16)	119.2 (4)
N(1)C(2)C(21)	123.3 (2)	C(15)C(16)C(11)	118.3 (4)
C(3)C(2)C(21)	130.2 (3)	C(2)C(21)C(22)	121.6 (3)
C(2)C(3)C(4)	109.6 (2)	C(2)C(21)C(26)	119.8 (3)
C(2)C(3)N(3)	125.4 (3)	C(22)C(21)C(26)	118.5 (3)
N(3)C(3)C(4)	124.9 (2)	C(21)C(22)C(23)	120.6 (3)
C(3)C(4)C(5)	106.6 (2)	C(22)C(23)C(24)	120.2 (4)
C(4)C(5)N(1)	107.6 (3)	C(23)C(24)C(25)	119.8 (4)
C(4)C(5)C(51)	127.8 (3)	C(24)C(25)C(26)	120.4 (4)
N(1)C(5)C(51)	124.5 (2)	C(25)C(26)C(21)	120.4 (4)
C(3)N(3)C(6)	119.9 (3)	N(3)C(31)C(32)	119.6 (3)
C(3)N(3)C(31)	119.1 (3)	N(3)C(31)C(36)	118.8 (3)
C(6)N(3)C(31)	120.9 (2)	C(32)C(31)C(36)	121.6 (3)
N(3)C(6)C(7)	127.9 (3)	C(31)C(32)C(33)	118.9 (4)
N(3)C(6)C(61)	115.6 (3)	C(32)C(33)C(34)	120.3 (4)
C(7)C(6)C(61)	116.4 (3)	C(33)C(34)C(35)	120.1 (4)
C(6)C(7)C(71)	126.0 (3)	C(34)C(35)C(36)	120.7 (5)
C(6)C(7)C(72)	119.3 (3)	C(35)C(36)C(31)	118.5 (4)
C(71)C(7)C(72)	114.7 (3)	C(5)C(51)C(52)	118.7 (3)
C(6)C(61)N(61)	176.6 (4)	C(5)C(51)C(56)	123.4 (3)
C(7)C(71)N(71)	172.7 (5)	C(52)C(51)C(56)	117.8 (3)
C(7)C(72)N(72)	177.9 (4)	C(51)C(52)C(53)	121.1 (3)
N(1)C(11)C(12)	118.6 (3)	C(52)C(53)C(54)	120.5 (3)
N(1)C(11)C(16)	119.4 (3)	C(53)C(54)C(55)	119.3 (4)
C(12)C(11)C(16)	121.9 (3)	C(54)C(55)C(56)	120.4 (3)
		C(55)C(56)C(51)	121.0 (4)

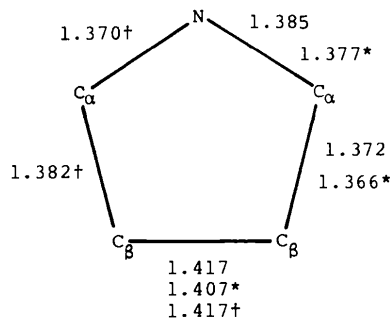


Fig. 2. A comparison of bond distances ( $\text{\AA}$ ) for the pyrrole ring as derived in this analysis with those for  $S(R,R)$ -v (Silverton & Lloyd, 1975) (marked with an asterisk), and with those determined by microwave spectroscopy (Nygaard *et al.*, 1969) (marked with a dagger).

generally favourably disposed for inter-ring conjugation. The lack of significant conjugation between pyrrole and its substituents in (I) is substantiated by the minor deviations from  $C_{2v}$  symmetry in its pyrrole-ring geometry in comparison with the large differences in similar bond distances (as great as  $0.065 \text{ \AA}$ ) which have been reported (Bonnett, Hursthouse & Neidle, 1972*a,b*) for pyrrole derivatives in which conjugation is obviously important. The differences within this structure and within that reported for  $S(R,R)$ -v are modest, generally within two e.s.d.'s (*ca*  $0.008 \text{ \AA}$ ).

In an effort to assess the effect of the substituents on the geometry of the pyrrole ring, some understanding of the inductive character of the substituents is necessary. An alkane group is generally characterized as an electron donor, a  $+I$  substituent (March, 1968), whereas a phenyl group is usually considered to be a weak electron-withdrawing group, a  $-I$  substituent. The  $N$ -substituent in  $S(R,R)$ -v is a phenyl-substituted alkane which displays  $+I$  character. Its electron-donating character is indicated by the endocyclic angle of the substituted C atom of the phenyl ring,  $116.9^{\circ}$  (Domenicano, Vaciago & Coulson, 1975). The  $C_{\alpha}$  substituent in  $S(R,R)$ -v may also be expected to be somewhat electron-donating, though the presence of a hydroxyl group on the substituent C atom may reduce its efficacy toward pyrrole. It therefore appears to be appropriate to classify the substituent effects on pyrrole as displaying a net  $+I$  character. The pyrrole ring in (I) is more highly substituted than in  $S(R,R)$ -v, and therefore the substituent effects might be expected to be more pronounced. This does not appear to be the case. In fact, the effects appear to be quite similar in that there is reason to believe that there is a net  $+I$  effect in (I) as well.

The criteria of Domenicano *et al.* (1975) for assessing the interactions of substituents and phenyl rings can be used in analysing the substituent effects between pyrrole and its phenyl rings. The appropriate phenyl endocyclic angles for the two pyrrole  $\alpha$  substituents [ $118.5 (3)$  and  $117.8 (3)^{\circ}$ ] are comparable with those tabulated for biphenyls (mean  $117.6^{\circ}$ ), and thus indicate that there is little inductive interaction between the pyrrole moiety and these phenyl substituents. In contrast, the comparable angle for the  $N$ -phenyl substituent [ $121.9 (3)^{\circ}$ ] is indicative of a strong  $+I$  effect for the pyrrole ring from its  $N$ -phenyl substituent. There is an indication that the  $\beta$  substituent at C(3) is significantly electron-withdrawing in that the  $C_{\alpha}C_{\beta}C'_{\beta}$  angle is greater than that for its unsubstituted neighbour. The electron-withdrawing character of the substituent at C(3) is further substantiated by the endocyclic angle of its phenyl ring,  $C(32)C(31)C(36) = 121.6 (3)^{\circ}$ . The near  $C_{2v}$  symmetry of the pyrrole ring indicates that the  $\beta$  substituent has little effect on the  $C_{\alpha}$ -N distances. It therefore seems reasonable to propose, at least with respect to the C-N bonds, that (I) and  $S(R,R)$ -v display similar  $+I$  inductive effects and that they are responsible for the differences in the  $C_{\alpha}$ -N and  $C_{\alpha}$ - $C_{\beta}$  distances for the pyrrole ring as determined by X-ray crystallography and microwave spectroscopy.

The second principal functional group of (I), the aniline moiety, is capable of greatly differing substituent interactions depending on the nature of the substituent(s) and on the position(s) of substitution. (I) has an  $N,N$ -disubstituted aniline as a bridging group between the pyrrole moiety and a tricyanovinyl group. Numerous crystal-structure analyses of  $N$ -substituted anilines have been reported and it can be readily

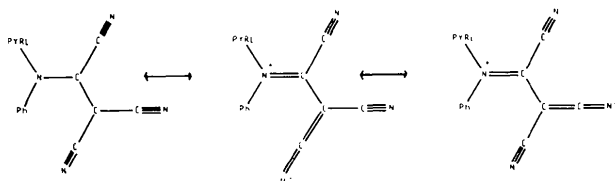


Fig. 3. Canonical form contributing to the resonance structure of the 3-(*N*-phenyl-*N*-tricyanovinyl) moiety (PYRL = pyrrole).

Table 7. *Interatomic contacts (Å) between carbon and nitrogen atoms less than 3.5 Å*

C(13)–C(13')	3.222	C(5)–N(72)	3.320
C(15)–C(15')	3.246	N(1)–N(72)	3.336
C(33)–C(33')	3.276	C(53)–N(72)	3.423
C(35)–C(35')	3.284	C(34)–N(61)	3.471
		C(33)–C(34)	3.472

demonstrated that the geometry of the amino N is generally sensitive to the substituent interactions. For example, in *N*(diphenylmethylene)aniline (Tucker, Hoekstra, ten Cate & Vos, 1975) the geometry of the amine group is characterized by a  $sp^2$  N atom double-bonded to the methylene C atom with C–N = 1.287 Å; there is no evidence for significant conjugation between the N atom and the phenyl group of the aniline moiety. The aniline moiety in *N*-methyl-2-(*N*-methylamino)-3,5-dinitrobenzamide (Mathew & Palenik, 1974) displays conjugation between its amino N atom and the substituted phenyl ring (C–N = 1.343 Å), while 1-(*N*-fluoro-*N*-*tert*-butyl)amino-2,4,6-trinitrobenzene (Batail, Grandjean, Dudragne & Michaud, 1974), in which the *N*-substituents are not suitable for  $\pi$  bonding, shows no significant conjugation.

The orientation of the aniline *N*-substituents in (I) (Fig. 1 and Table 4) are most favourable for conjugation between the amine N and the tricyanovinyl group. The presence of such conjugation is readily confirmed by an examination of the C–N and C–C distances. N(3)–C(6), 1.347 Å, is clearly indicative of significant double-bond character (Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1972), while C(6)–C(7), 1.376 Å, is comparable to that for the  $C_\alpha$ – $C_\beta$  bonds in the pyrrole ring and is thus also indicative of a resonance structure. The canonical forms contributing to such a structure are presented in Fig. 3. The terminal cyano groups, C(71)N(71) and C(72)N(72) in Fig. 1, are involved in the conjugation; consequently, their bond distances should also reflect the resonance structure. This is clearly the case in that both C(7)–C(71) and C(7)–C(72) are shorter than C(6)–C(61). Furthermore, C(71)–N(71) and C(72)–N(72) are longer than C(61)–N(61) both before and after riding-motion corrections (Busing &

Levy, 1964; Busing, Martin & Levy, 1964). In general, these bond distances are comparable with those reported for 3-amino-3-chloro-2-cyanoacrylic acid anilide (Block, Löckenhoff & Allmann, 1975) in which somewhat analogous conjugation has been reported.

The intermolecular contacts less than 3.5 Å are presented in Table 7. (I) contains no H atoms suitable for hydrogen bonding and the distances displayed in Table 7 present no unusually short non-bonded contacts. It seems reasonable to conclude that intermolecular interactions are confined to van der Waals forces.

The author thanks Professor R. R. Schmidt for the crystals and the Institut für Organische Chemie, Biochemie und Isotopenforschung der Universität Stuttgart for making this work possible.

### References

- BATAIL, P., GRANDJEAN, D., DUDRAGNE, F. & MICHAUD, C. (1974). *Acta Cryst.* **B30**, 2653–2658.
- BLOCK, H. D., LÖCKENHOFF, H.-D. & ALLMANN, R. (1975). *Cryst. Struct. Commun.* **4**, 77–80.
- BONNETT, R., HURSTHOUSE, M. B. & NEIDLE, S. (1972a). *J. Chem. Soc. Perkin II*, pp. 902–906.
- BONNETT, R., HURSTHOUSE, M. B. & NEIDLE, S. (1972b). *J. Chem. Soc. Perkin II*, pp. 1335–1340.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-TM-3794. Oak Ridge National Laboratory, Tennessee.
- KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, M. W., MOTHERWELL, W. D. S., PETTERSEN, R. C. & TOWN, W. G. (1972). *Molecular Structures and Dimensions*, Vol. A1, p. S2. Utrecht: Oosthoek.
- LEMLEY, J. T., SKARSTAD, P. M. & HUGHES, R. E. (1976). *Acta Cryst.* **B32**, 35–40.
- MARCH, J. (1968). *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, pp. 19–21. New York: McGraw-Hill.
- MATHEW, M. & PALENIK, G. J. (1974). *Acta Cryst.* **B30**, 2381–2385.
- NYGAARD, L., NIELSEN, J. T., KIRCHHEINER, J., MALTESEN, G., RASTRUP-ANDERSEN, J. & SØRENSEN, G. O. (1969). *J. Mol. Struct.* **3**, 491–506.
- SILVERTON, J. V. & LLOYD, H. A. (1975). *Acta Cryst.* **B31**, 1576–1581.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- TUCKER, P. A., HOEKSTRA, A., TEN CATE, J. M. & VOS, A. (1975). *Acta Cryst.* **B31**, 733–737.