

The Crystal and Molecular Structure of 5-Dicyanomethylene-2,4-di(1-pyrrolidinyl)-3-pyrrolecarbonitrile

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(Received 18 July 1978; accepted 1 September 1978)

Abstract

The structure of $C_{16}H_{16}N_6$ (I) has been determined for a crystal cooled to *ca* 120 K. The space group is $P2_1/c$ with $a = 9.889$ (2), $b = 8.466$ (1), $c = 17.322$ (2) Å, $\beta = 99.81$ (1)°, $Z = 4$. The structure was refined with 10 514 unique reflections to $R = 0.049$ and $R_w = 0.062$. (I) is a pyrrole derivative in which the N atom is devoid of an exocyclic substituent but in which all C atoms are substituted. Each of the pyrrole exocyclic bonds displays some degree of double-bond character. There is pronounced intramolecular steric repulsion between the dicyanomethylene moiety and the adjacent pyrrolidinyl substituent which significantly affects the geometry of the pyrrolidinyl N atom. The relative contributions of various canonical forms to the resonance structure of (I) are assessed. The influence of packing interactions on the charge distribution within the cyano groups of the dicyanomethylene moiety is examined.

Introduction

The structure analysis of the title compound (I) was undertaken to determine its chemical structure, which was found to be that of a derivative of a pyrrole in which the N atom carries no substituent. This tautomeric form of pyrrole, which is also found as a subunit in porphine derivatives, is apparently stabilized in (I) by some degree of double-bond character with substituents on each of the pyrrole C atoms. The observed geometry provides a basis for some insight into the relative distribution of double-bond character in each of these exocyclic bonds.

Experimental

(I) crystallized from acetonitrile in space group $P2_1/c$ with $Z = 4$. All crystallographic data, for a crystal $0.3 \times 0.5 \times 0.5$ mm contained in a thin-walled glass capillary, were measured with a Syntex PI auto-

diffractometer equipped with a low-temperature device (Syntex LT-1) operating at *ca* 120 K. Lattice parameters [$a = 9.889$ (2), $b = 8.466$ (1), $c = 17.322$ (2) Å, $\beta = 99.81$ (1)°] resulted from a least-squares† refinement (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) with the 2θ values for 67 automatically centered reflections in the angular range $30.2 < 2\theta < 42.7^\circ$ (monochromatized Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å); $\rho_c = 1.359$ Mg m⁻³. Intensities were measured in an ω -scan mode to a resolution of $2\theta_{\max} = 90^\circ$. The scan rate varied from 2.0 to 24.0° min⁻¹; the scan range was 0.75° and background was counted on each side of the reflection center ($\Delta\omega = 1.0^\circ$) for one half the scan time. 11 786 unique reflections were measured, 8213 of which were classified as observed with $I > 2\sigma(I)$. Data were corrected for Lorentz and polarization effects and for a systematic decrease in the

† Unless otherwise indicated, the XRAY system (Stewart *et al.*, 1976) was used for all computerized calculations.

Table 1. Fractional atomic coordinates ($\times 10^5$) for the C and N atoms with *e.s.d.*'s

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	66444 (7)	-4283 (9)	19480 (4)
C(2)	78303 (8)	2261 (9)	23265 (4)
C(3)	78776 (8)	3391 (10)	31684 (4)
C(4)	66939 (8)	-4323 (9)	33118 (4)
C(5)	58897 (8)	-7522 (9)	25013 (4)
C(6)	45224 (8)	-11907 (10)	22890 (5)
C(7)	40123 (9)	-14527 (11)	14751 (5)
N(7)	35659 (9)	-16830 (11)	8233 (5)
C(8)	35092 (8)	-11347 (11)	27744 (5)
N(8)	26337 (8)	-10571 (11)	31395 (5)
C(9)	89207 (9)	10912 (11)	37014 (5)
N(9)	97834 (9)	17624 (12)	41062 (5)
N(41)	63726 (7)	-8916 (9)	39904 (4)
N(21)	87735 (7)	6709 (9)	19228 (4)
C(42)	72669 (9)	-4925 (11)	47482 (5)
C(43)	67336 (10)	-15448 (11)	53435 (5)
C(44)	62458 (10)	-29994 (11)	48562 (5)
C(45)	54813 (9)	-22571 (10)	41062 (5)
C(22)	101284 (9)	13433 (11)	22422 (5)
C(23)	108735 (10)	12364 (13)	15408 (6)
C(24)	97274 (11)	15622 (13)	8504 (6)
C(25)	85500 (10)	5826 (12)	10558 (5)

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intensities of three reference reflections which reached *ca* 20% by the end of data collection.

The structure was solved by direct methods and refined by block-diagonal least squares. The blocks were: scale factor or isotropic extinction correction plus the variables of N(1), C(2), C(3); C(4), C(5), C(6); C(7), N(7), C(8); N(8), C(9), N(9); N(21), N(41); the remaining eight blocks consisted of the variables of one pyrrolidiny C atom and its H atoms. All coordinates, anisotropic temperature factors for C and N, isotropic temperature factors for H, a single scale factor and an isotropic extinction correction were refined. In addition to the observed data, those for which the calculated intensity was greater than the cut-off value were included. In this manner 10 514 reflections contributed to the refinement of 264 variables to give $R = 0.049$

and $R_w = 0.062$ for which $w = [\sigma^2(F) + 0.0125|F| + 0.0001|F|^2]^{-1}$; the e.s.d. of an observation of unit weight is 1.53.*

Results and discussion

Atomic coordinates for C and N atoms are presented in Table 1, coordinates and isotropic temperature factors for H atoms in Table 2, and bond distances and angles between C and N atoms in Table 3. The isotropic extinction coefficient, g , refined to 4.96×10^{-5} . A stereoscopic projection (Johnson, 1971) of (I) is presented with the atom labelling in Fig. 1.

The geometry of (I) provides evidence in support of double-bond character in each of the exocyclic bonds to the pyrrole moiety. There is also considerable intramolecular steric repulsion between the pyrrole substituents, particularly between those bonded to C(4) and C(5). Since these interactions may be expected to

Table 2. Fractional atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^2$) for the H atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
H(421)	7231 (16)	652 (20)	4845 (9)	2.2
H(422)	8177 (17)	-769 (20)	4700 (10)	2.6
H(431)	5962 (17)	-1051 (20)	5534 (10)	2.8
H(432)	7426 (17)	-1754 (22)	5805 (10)	2.6
H(441)	5678 (17)	-3691 (20)	5093 (10)	2.9
H(442)	7064 (17)	-3639 (20)	4748 (9)	2.5
H(451)	4571 (17)	-1887 (21)	4195 (9)	3.2
H(452)	5342 (16)	-2937 (20)	3631 (9)	2.5
H(222)	10555 (16)	747 (19)	2698 (9)	2.6
H(221)	9999 (16)	2469 (19)	2389 (9)	1.9
H(231)	11655 (18)	2016 (23)	1597 (10)	3.1
H(232)	11212 (18)	165 (22)	1497 (10)	3.5
H(241)	9440 (18)	2675 (22)	838 (10)	3.4
H(242)	9951 (19)	1282 (21)	316 (10)	3.3
H(251)	8614 (17)	-545 (20)	905 (10)	2.5
H(252)	7624 (18)	994 (21)	849 (10)	2.7

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33883 (57 pp.). Copies may be obtained through The Executive Secretary International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

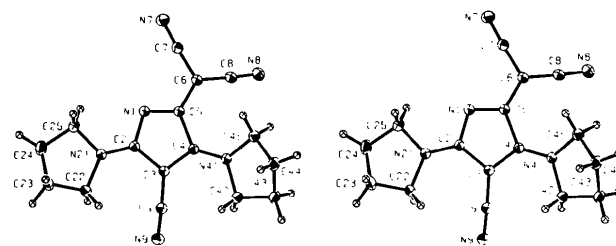


Fig. 1. A stereoscopic view of (I) showing the numbering scheme.

Table 3. Bond distances (Å) and angles (°) between C and N atoms with e.s.d.'s

Bond distances corrected for riding motion (Busing & Levy, 1964; Busing, Martin & Levy, 1964) are given in square brackets.

N(1)—C(2)	1.360 (1)	C(5)—C(6)	1.390 (1)	N(41)—C(42)	1.491 (1)		
N(1)—C(5)	1.340 (1)	C(6)—C(7)	1.431 (1) [1.433]	N(41)—C(45)	1.488 (1)		
C(2)—C(3)	1.454 (1)	C(6)—C(8)	1.414 (1) [1.415]	C(22)—C(23)	1.527 (2)		
C(3)—C(4)	1.399 (1)	C(7)—N(7)	1.157 (1) [1.159]	C(23)—C(24)	1.526 (1)		
C(4)—C(5)	1.515 (1)	C(8)—N(8)	1.158 (1) [1.159]	C(24)—C(25)	1.520 (2)		
C(2)—N(21)	1.313 (1)	C(9)—N(9)	1.157 (1) [1.159]	C(42)—C(43)	1.523 (1)		
C(4)—N(41)	1.327 (1)	N(21)—C(22)	1.474 (1)	C(43)—C(44)	1.524 (1)		
C(3)—C(9)	1.413 (1) [1.416]	N(21)—C(25)	1.482 (1)	C(44)—C(45)	1.523 (1)		
C(2)N(1)C(5)	106.16 (7)	C(5)C(4)N(41)	126.95 (7)	C(6)C(8)N(8)	176.48 (9)	N(21)C(22)C(23)	102.09 (7)
N(1)C(2)C(3)	112.82 (7)	C(4)C(5)N(1)	110.97 (7)	C(3)C(9)N(9)	176.36 (10)	C(22)C(23)C(24)	102.60 (8)
N(1)C(2)N(21)	119.52 (7)	C(4)C(5)C(6)	128.77 (8)	C(2)N(21)C(22)	126.43 (7)	C(23)C(24)C(25)	102.36 (8)
C(3)C(2)N(21)	127.66 (7)	N(1)C(5)C(6)	120.05 (7)	C(2)N(21)C(25)	121.91 (7)	C(24)C(25)N(21)	102.81 (7)
C(2)C(3)C(4)	105.21 (6)	C(5)C(6)C(7)	117.76 (8)	C(22)N(21)C(25)	111.64 (7)	N(41)C(42)C(43)	103.98 (7)
C(2)C(3)C(9)	125.44 (7)	C(5)C(6)C(8)	126.11 (7)	C(4)N(41)C(42)	121.18 (7)	C(42)C(43)C(44)	102.18 (7)
C(4)C(3)C(9)	129.34 (8)	C(7)C(6)C(8)	115.11 (7)	C(4)N(41)C(45)	125.72 (7)	C(43)C(44)C(45)	101.73 (7)
C(3)C(4)C(5)	104.00 (7)	C(6)C(7)N(7)	178.01 (10)	C(42)N(41)C(45)	109.48 (7)	C(44)C(45)N(41)	102.49 (7)
C(3)C(4)N(41)	128.89 (7)						

influence the relative distribution of exocyclic double bonds, they will be examined prior to attempting to assess the relative contribution of various canonical forms to the resonance structure.

N(41) is that most strongly affected. Like N(21), N(41) is sp^2 hybridized, but, unlike N(21), its geometry is distorted from ideality, the sum of its bond angles being 356.4° [$\sum \text{CN}(21)\text{C} = 360.0^\circ$]. The e.s.d.'s for mean planes calculated for each of these N atoms and the C atoms bonded to it are 0.078 and 0.006 Å respectively. It can be seen from Fig. 1 that the distortion in the geometry of N(41) arises from steric interaction. This observation is confirmed by the dihedral angles: $\text{C}(5)\text{C}(4)\text{N}(41)\text{C}(42) = 179.9(1)$, $\text{C}(5)\text{C}(4)\text{N}(41)\text{C}(45) = 23.6(1)$, $\text{C}(6)\text{C}(5)\text{C}(4)\text{N}(41) = 18.9(1)$, $\text{C}(3)\text{C}(4)\text{C}(5)\text{N}(1) = 9.3(1)$, $\text{C}(4)\text{C}(5)\text{C}(6)\text{C}(7) = -178.8(1)$ and $\text{C}(4)\text{C}(5)\text{C}(6)\text{C}(8) = 13.3(1)^\circ$; it is further substantiated by the bond angles in Table 3. The bond angles also indicate that there is steric repulsion between the cyano group at C(3) and its neighboring pyrroldinyl groups. The e.s.d. for the mean plane through the five pyrrole atoms is 0.04 Å, that for the pyrrole atoms plus their bonded

atoms is 0.15 Å, and that for the plane through C(5) and the dicyanomethylene substituent is 0.05 Å.

The structure of (I) is attributable to contributions from several canonical forms. The unusual unsubstituted character of the pyrrole N atom implies that each contributing canonical form has an endocyclic double bond to this atom (Fig. 2). The bond distances indicate that the relative double-bond character in chemically equivalent bonds follows the trend: $\text{C}(2)\text{--N}(21) > \text{C}(4)\text{--C}(41)$, $\text{C}(5)\text{--N}(1) > \text{C}(2)\text{--N}(1)$, $\text{C}(5)\text{--C}(6) \simeq \text{C}(3)\text{--C}(4)$, $\text{C}(3)\text{--C}(9) \sim \text{C}(6)\text{--C}(8) > \text{C}(6)\text{--C}(7)$ and $\text{C}(2)\text{--C}(3) \gg \text{C}(4)\text{--C}(5)$. This sequence is consistent with the series for the canonical forms: $|(\text{Ia}) + (\text{Ib})| > |(\text{Ic}) + (\text{Id})| > (\text{Ie}) \gg (\text{If})$; that canonical form (If) makes only a minor (if any) contribution to the resonance structure is not surprising since it is formally a diradical.

A feature of the structure of (I) is the implication of the bond distances with respect to possible canonical forms of the dicyanomethylene moiety of (Ia), (Ib), and (Ie) (Fig. 3). If the indicated resonance within this moiety occurs, as it apparently does in TCNQ salts, the $\text{C}(6)\text{--C}(7)$ and $\text{C}(6)\text{--C}(8)$ distances should be very similar; clearly (Table 3) this is not the case. Comparison of the observed values for (I) with those of Herbstein (1971) for $(\text{TCNQ})^0$, $(\text{TCNQ})^{0.5-}$, and $(\text{TCNQ})^{1-}$ indicates that the C(7) cyano group carries almost no negative charge [$\text{C--C} = 1.434(4)$ Å in $(\text{TCNQ})^0$ and $1.431(2)$ Å in $(\text{TCNE})^0$ (Becker, Coppens & Ross, 1973)], whereas the C(8) and C(9) cyano groups carry negative charge at least equivalent to that in the cyano groups of $(\text{TCNQ})^{1-}$ [$\text{C--C} = 1.417(4)$ Å]. Thus one must conclude that the contribution to the observed structure of (I) is $(\text{Ia}, \text{b}, \text{e}) \gg (\text{I}'\text{a}, \text{b}, \text{e})$.

Crystal-packing (Fig. 4 and Table 4) effects may account for the above observations. The C(8) cyano group is in close contact with C(2) and N(21) of a symmetry-related molecule. The $\text{N}(8)\cdots\text{N}(21)$ distance is only 3.094 Å and $\text{N}(8)\cdots\text{C}(2)$ is 3.262 Å. This packing arrangement obviously stabilizes canonical forms (Ia) and (Ib) because of the proximity of the

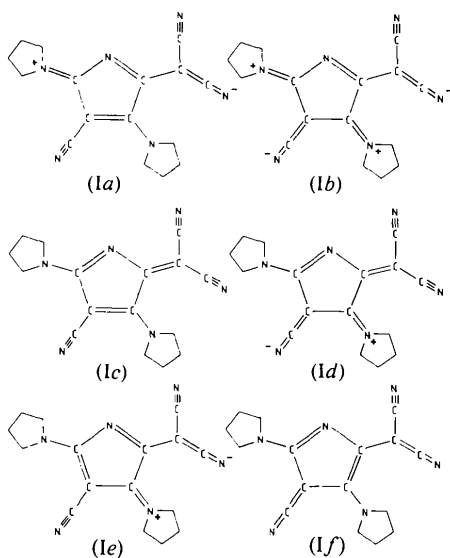


Fig. 2. Canonical forms of (I).

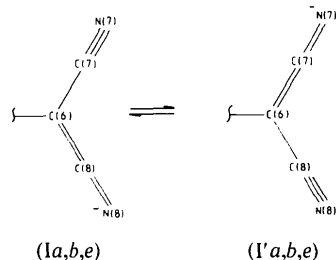


Fig. 3. Canonical forms of the dicyanomethylene moiety.

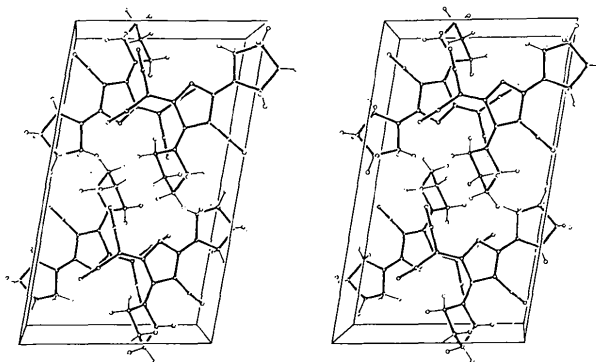


Fig. 4. A stereoscopic view of the crystal packing.

Table 4. *Non-bonded intermolecular contacts* (Å)

N(1)...C(8)	3.673	N(7)...C(42)	3.433
C(2)...C(8)	3.347	N(7)...C(44)	3.379, 3.350
C(2)...N(8)	3.262	N(8)...N(21)	3.094
C(3)...C(7)	3.413	N(8)...C(22)	3.482, 3.372
C(3)...N(7)	3.506	N(8)...C(23)	3.581
C(4)...C(7)	3.473	N(8)...C(24)	3.737
C(4)...N(7)	3.538	N(8)...C(25)	3.459
N(7)...C(9)	3.311	N(8)...C(43)	3.404
N(7)...N(9)	3.585	C(25)...C(44)	3.561
N(7)...N(41)	3.577		

oppositely charged N atoms; it also accounts for the preferential charge distribution within the dicyanomethylene moiety. With this in mind, there is reason to believe that the resonance structure of (I) in solution may differ from that in the crystal. The possibility that intermolecular charge transfer between substituents in crystalline (I) occurs also merits investigation.

Codding & Tulinsky (1972) have reported that porphine, tetraphenylporphine and $\alpha,\beta,\gamma,\delta$ -tetra-*n*-propylporphine free bases show very similar geometries in the macrocyclic ring and have presented average bond distances for these structures. The averages appropriate for comparison with (I) are: $N-C_{\alpha} = 1.372$ (10), $C_{\alpha}-C_{\beta} = 1.451$ (9) and $C_{\beta}-C_{\beta'} = 1.345$ (3) Å (subscripts indicate ring atom position relative to the pyrrole N atom and chemical

equivalence). Comparison of these values with those in (I) illustrates the sensitivity of the bond distances within this pyrrole tautomer to the electronic character of the substituents.

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

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