

Ces liaisons hydrogène sont caractérisées par:

– les distances: N(1)–N(27ⁱ) 3,080 (3); N(3)–OXYⁱ 2,808 (3); N(7)–OXY 2,699 (3); et N(23)–OXYⁱⁱ 2,828 (4) Å;

– les angles: N(1)–H(N27ⁱ)–N(27ⁱ) 158; N(3)–H(OXBⁱ)–OXYⁱ 164; et N(23)–H(OXAⁱⁱ)–OXYⁱⁱ 175°;

avec le code de symétrie: (i) $1 + x, y, z$ et (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Rappelons que dans les variétés monocliniques I et II, les doublets libres des atomes N(3) n'interviennent pas dans les liaisons hydrogène. D'autre part, il existe de nombreuses liaisons de van der Waals qui contribuent à la bonne cohésion du cristal.

En conclusion, l'adjonction du cycle pyrimidinique ne modifie pas l'aptitude du dihydrocarbazole à la formation de complexes par transfert de charge. Il est probable que la conformation du noyau cyclohexadiényle-1,3 n'entraîne pas de perturbations importantes puisque ce dernier cycle évolue d'une conformation demi-chaise vers une quasi-planéité, comme nous avons pu le montrer dans les différentes études structurales antérieures de ce tétrahétérocycle.

L'organisation structurale de type alterné, ainsi que le degré de transfert de charge voisin de zéro permettent de prévoir un comportement électrique isolant pour le composé cité en titre.

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Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarbonitrile

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Abstract. C₉H₆N₂, $M_r = 142.16$, triclinic, $P\bar{1}$, $a = 7.693$ (1), $b = 8.400$ (1), $c = 12.239$ (1) Å, $\alpha = 73.98$ (1), $\beta = 89.59$ (1), $\gamma = 75.51$ (1)°, $V = 734.4$ (2) Å³, $Z = 4$, $D_x = 1.286$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.743$ cm⁻¹, $F(000) = 296$, $T = 295$ K. The structure was solved by symbolic addition and refined to final $R = 0.054$ for 2208 observed

reflections [$I > 3\sigma(I)$]. There are two molecules in the asymmetric unit. The range of the C–C–C angles, between 58.3 (2) and 130.8 (2)°, in contrast to the tetrahedral angle (109.5°), indicates that the title compound is a strained organic molecule. The electron-withdrawing cyano groups show characteristic influences on the cyclopropane bonds.

Table 1. Atomic coordinates and thermal parameters

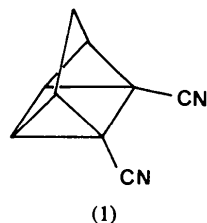
 U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(\text{\AA}^2 \times 10^3)$
N(1)	0.8876 (3)	-0.1179 (3)	0.3102 (2)	73 (2)
N(2)	1.3847 (3)	-0.1753 (3)	0.5153 (2)	69 (2)
C(1)	1.0158 (3)	0.1314 (3)	0.3202 (2)	43 (1)
C(2)	0.9165 (3)	0.3198 (3)	0.2994 (2)	49 (2)
C(3)	0.9796 (3)	0.3866 (3)	0.3894 (2)	51 (2)
C(4)	1.1746 (3)	0.2877 (3)	0.4043 (2)	46 (2)
C(5)	1.1887 (3)	0.1102 (3)	0.3909 (2)	42 (1)
C(6)	1.2372 (3)	0.2506 (3)	0.2968 (2)	52 (2)
C(7)	1.0658 (3)	0.2726 (3)	0.2259 (2)	52 (2)
C(8)	0.9418 (3)	-0.0043 (3)	0.3126 (2)	48 (2)
C(9)	1.2992 (3)	-0.0462 (3)	0.4600 (2)	50 (2)
N(1')	0.1187 (3)	0.2744 (3)	0.9434 (2)	76 (2)
N(2')	0.6112 (4)	0.3090 (4)	1.1108 (2)	93 (2)
C(1')	0.4242 (3)	0.2501 (3)	0.8564 (2)	45 (1)
C(2')	0.4591 (3)	0.2840 (3)	0.7300 (2)	50 (2)
C(3')	0.5958 (3)	0.3866 (3)	0.7048 (2)	55 (2)
C(4')	0.7110 (3)	0.3109 (3)	0.8126 (2)	59 (2)
C(5')	0.5934 (3)	0.2679 (3)	0.9123 (2)	51 (2)
C(6')	0.7065 (4)	0.1297 (4)	0.8644 (2)	68 (2)
C(7')	0.5394 (4)	0.1118 (3)	0.8095 (2)	62 (2)
C(8')	0.2539 (3)	0.2641 (3)	0.9022 (2)	52 (2)
C(9')	0.6083 (4)	0.2921 (3)	1.0209 (2)	65 (2)

Table 2. Interatomic distances (\AA) and interatomic angles ($^\circ$)

N(1)—C(8)	1.141 (4)	N(1')—C(8')	1.146 (3)
N(2)—C(9)	1.146 (3)	N(2')—C(9')	1.148 (4)
C(1)—C(8)	1.420 (4)	C(1')—C(8')	1.413 (3)
C(1)—C(2)	1.526 (3)	C(1')—C(2')	1.528 (3)
C(1)—C(5)	1.537 (3)	C(1')—C(5')	1.533 (4)
C(1)—C(7)	1.534 (3)	C(1')—C(7')	1.520 (3)
C(2)—C(3)	1.500 (4)	C(2')—C(3')	1.498 (4)
C(2)—C(7)	1.496 (3)	C(2')—C(7')	1.485 (3)
C(3)—C(4)	1.507 (3)	C(3')—C(4')	1.484 (3)
C(4)—C(5)	1.522 (3)	C(4')—C(5')	1.530 (4)
C(4)—C(6)	1.484 (3)	C(4')—C(6')	1.488 (4)
C(5)—C(9)	1.415 (3)	C(5')—C(9')	1.409 (4)
C(5)—C(6)	1.524 (3)	C(5')—C(6')	1.520 (4)
C(6)—C(7)	1.527 (4)	C(6')—C(7')	1.513 (4)
C(2)—C(1)—C(5)	104.2 (2)	C(2')—C(1')—C(5')	104.5 (2)
C(7)—C(1)—C(2)	58.6 (1)	C(7')—C(1')—C(2')	58.3 (1)
C(2)—C(1)—C(8)	127.2 (2)	C(2')—C(1')—C(8')	125.8 (2)
C(5)—C(1)—C(7)	89.8 (2)	C(5')—C(1')—C(7')	90.1 (2)
C(5)—C(1)—C(8)	125.3 (2)	C(5')—C(1')—C(8')	125.9 (2)
C(7)—C(1)—C(8)	130.2 (2)	C(7')—C(1')—C(8')	130.8 (2)
C(1)—C(2)—C(3)	109.3 (2)	C(1')—C(2')—C(3')	108.7 (2)
C(1)—C(2)—C(7)	61.0 (1)	C(7')—C(2')—C(1')	60.6 (2)
C(3)—C(2)—C(7)	110.8 (2)	C(3')—C(2')—C(7')	110.6 (2)
C(2)—C(3)—C(4)	99.2 (2)	C(2')—C(3')—C(4')	99.7 (2)
C(3)—C(4)—C(5)	109.1 (2)	C(3')—C(4')—C(5')	109.4 (2)
C(3)—C(4)—C(6)	110.8 (2)	C(3')—C(4')—C(6')	110.7 (3)
C(5)—C(4)—C(6)	60.9 (2)	C(5')—C(4')—C(6')	60.5 (2)
C(1)—C(5)—C(4)	104.4 (2)	C(1')—C(5')—C(4')	103.8 (2)
C(1)—C(5)—C(6)	89.9 (2)	C(1')—C(5')—C(6')	89.2 (2)
C(1)—C(5)—C(9)	126.1 (2)	C(1')—C(5')—C(9')	125.9 (2)
C(6)—C(5)—C(4)	58.3 (2)	C(6')—C(5')—C(4')	58.4 (2)
C(4)—C(5)—C(9)	126.1 (2)	C(4')—C(5')—C(9')	127.6 (3)
C(6)—C(5)—C(9)	130.1 (2)	C(6')—C(5')—C(9')	129.3 (2)
C(4)—C(6)—C(5)	60.8 (2)	C(4')—C(6')—C(5')	61.1 (2)
C(4)—C(6)—C(7)	105.1 (2)	C(4')—C(6')—C(7')	105.2 (2)
C(5)—C(6)—C(7)	90.5 (2)	C(5')—C(6')—C(7')	90.8 (2)
C(2)—C(7)—C(1)	60.4 (1)	C(1')—C(7')—C(2')	61.1 (1)
C(1)—C(7)—C(6)	89.9 (2)	C(1')—C(7')—C(6')	90.0 (2)
C(2)—C(7)—C(6)	104.5 (2)	C(2')—C(7')—C(6')	104.7 (2)
N(1)—C(8)—C(1)	177.0 (2)	N(1')—C(8')—C(1')	177.4 (3)
N(2)—C(9)—C(5)	177.8 (3)	N(2')—C(9')—C(5')	176.0 (3)

Introduction. Within a project of determining the bonding systems of polycyclic small-membered rings and the electronic influences of substituents on the molecular dimensions of these compounds (Iringtanger, Goldmann, Jahn, Nixdorf, Rodewald, Malsch & Maier, 1984) we established the structure of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarbonitrile (1).



Experimental. Colourless needle $0.4 \times 0.3 \times 0.25$ mm, crystallized from 2-propanol solution (Edman, 1967). Data measured on CAD-4 diffractometer (Enraf-Nonius); ω - 2θ scan method; cell dimensions from 2θ angles of 25 reflections ($16 < 2\theta < 38^\circ$); 3520 data up to $\sin \theta/\lambda = 0.66 \text{ \AA}^{-1}$; $0 < h < 10$, $-10 < k < 11$, $-16 < l < 16$; 3 standard reflections $3\bar{1}5$, $34\bar{1}$, $2\bar{5}8$ (max. variation 0.979 to 1.0); 2208 intensities with $I > 3\sigma(I)$. Because of extinction 3 reflections excluded (101 , $11\bar{1}$, $11\bar{1}$). $R_{int} = 0.013$. Structure solution with *MULTAN80* failed (*MULTAN80*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Successful solution with *SIMPEL83* (Schenk & Kiers, 1984), in default run. 7 symbols used and correct solution found from 124 possible ones with a combined

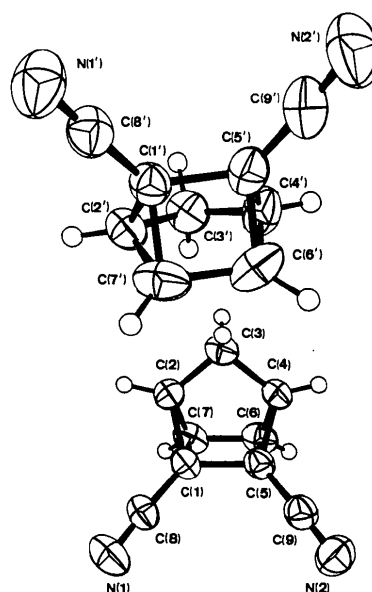


Fig. 1. ORTEP plot (Johnson, 1970) of both independent molecules of (1), with 50% probability thermal ellipsoids, showing the numbering system.

FOM consisting of the triplet consistency, the positive quartet consistency, negative quartet criterion, the Harker-Kasper criterion and the \sum_1 criterion. In a subsequent 'map' the solution with the best value of CFOM revealed all atoms of both independent molecules. Surprisingly, the negative quartet criterion alone behaved very poorly; however, its negative effect was compensated by the positive quartet FOM. Structure refined by full-matrix least squares on F^2 ; anisotropic thermal parameters for C and N atoms; H atoms located by difference Fourier syntheses and refined isotropically. 247 parameters, $R = 0.054$ for 2208 observed reflections, $wR = 0.076$, $w = 4F^2/\sigma^2(F^2) + (0.03 F^2)^2$, $S = 3.062$; $\Delta/\sigma_{\max} < 0.01$; largest peak = $0.19 \text{ e } \text{\AA}^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974); SDP programs (Frenz, 1978) used on PDP 11/44, SIMPEL83 used on a Vax 11/730.

Discussion. The final atomic parameters are given in Table 1.* Bond lengths and bond angles of (1) are listed in Table 2. The numbering system of (1) is depicted in Fig. 1. Table 3 gives the values of the differences from the averaged cyclopropane bonds in comparison with cyclopropanecarbonitrile (2a) and (2b) [(2a) X-ray structure by Kiers, de Boer, Heijdenrijk, Stam & Schenk (1985); (2b) microwave study by Pearson, Choplin & Laurie (1975)].

The cyclopropane rings of (1) show the typical shortening of the distal bond and the lengthening of the vicinal bonds caused by the acceptor properties of the cyano groups. (Allen, 1980) The averaged difference values of (1) are in good agreement with the values of (2a).

As a further consequence of the interaction between the cyano groups and the three-membered rings the C \equiv N triple bonds [1.145 (3) Å] are lengthened and the C—CN single bonds [1.414 (5) Å; Table 2] are significantly shortened compared with open-chain saturated compounds (Allen, 1981). The C \equiv N bond lengths compare well with the lengths in (2a) and also in 1,5,6-trimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarbonitrile (Maeda, Terauchi, Nakatsu, Yoshida, Asako, Miki & Yamada, 1983).

In the cyclobutane ring of (1) the C(1)—C(5) [1.537 (3) Å] and the C(1')—C(5') [1.533 (4) Å] bonds are longer than the C(6)—C(7) [1.527 (4) Å] and the C(6')—C(7') [1.513 (4) Å] bonds. These differences are produced by the short contacts C(8)...C(9) [3.190 (3) Å] and C(8')...C(9') [3.189 (4) Å] respec-

* Lists of H-atom bond distances, angles and atomic positions, anisotropic thermal parameters, a list of structure amplitudes and a figure showing the packing arrangement along a have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42795 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Influence of the cyano groups on the bond lengths of the three-membered rings

Averaged bond lengths and averaged standard deviations (Å) are given.

Compound*	Mean bond length, three-membered ring	Δ			C—CN	C \equiv N
		distal bond	vicinal bond 1	vicinal bond 2		
(1)	C(1)/C(2)/C(7)					
	1.519 (3)	-0.023	+0.007	+0.015	1.420 (4)	1.141 (4)
	C(4)/C(5)/C(6)					
	1.510 (3)	-0.025	+0.012	+0.014	1.415 (3)	1.146 (3)
	C(1')/C(2')/C(7')					
	1.511 (3)	-0.026	+0.017	+0.009	1.413 (3)	1.146 (3)
	C(4')/C(5')/C(6')					
	1.513 (4)	-0.025	+0.017	+0.007	1.409 (4)	1.148 (4)
	Averaged values					
	1.513 (3)	-0.025	+0.013	+0.011	1.414 (4)	1.145 (4)
(2a)	1.498	-0.022	+0.011	+0.011	1.434 (2)	1.142 (2)
(2b)	1.519	-0.019	+0.009	+0.009		

* (1) Title compound; (2a) cyclopropanecarbonitrile, X-ray study; (2b) cyclopropanecarbonitrile, microwave study.

tively. The four-membered rings of (1) are planar within ± 0.001 Å. The dihedral angle between the three- and the four-membered rings is $107.0 (1)^\circ$ on average.

There are no short intermolecular contacts.

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