The Crystal and Molecular Structure of *N*-Ethylcarbazole†

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N-Ethylcarbazole crystallizes in the orthorhombic system, space group Pbca with fairly large unit cell dimensions of a=7.971(1), b=24.615(3), c=56.587(5) Å, D_m=1.17 g cm^{-3}, D_c=1.168 g cm^{-3} for Z=40. The structure was solved by the direct method and refined anisotropically by the least-squares procedure, R=0.062 for 5134 non-zero reflections. Five crystallographically independent molecules are not different from each other, the carbazole group is planar, and the ethyl group attached to the nitrogen atom is almost perpendicular to the carbazole ring. In the crystal, each carbazole ring makes a similar angle with the a axis [52 to 55°].

Recently, intrinsic and extrinsic photoconductivities of *N*-ethylcarbazole has been extensively studied by H. Mikawa and his co-workers[1] in conncetion with those of poly(*N*-vinylcarbazole).[2] In order to obtain a basic information to elucidate the correlation between the structure and photoconductivity, the crystal structure analysis of *N*-ethylcarbazole has been carried out.

Experimental

A large single crystal, grown from melt in a Bridgeman furnace,[3] was supplied by H. Mikawa and his co-workers of this university. A crystal with approximate dimensions of 0.3×0.35×0.31 mm was cut out and coated with collodion in order to prevent sublimation during the X-ray experiment.

The crystal was mounted on a Rigaku automated, four-circle diffractometer. Nickel-filtered Cu $K\alpha$ radiation was used. Unit-cell dimensions were determined by the least-squares fit of 2θ values of 22 high angle reflections.

Crystal Data: $C_{14}H_{13}N$, M=195.27, orthorhombic, space group Pbca (No. 61), a=7.791 (1), b=24.615 (3), c=56.587 (5) Å, V=11104 (2) Å^3, D_m=1.17 g cm^{-3} (by flotation in an aqueous solution of $ZnCl_2$), D_c=1.168 g cm^{-3} for Z=40, μ (Cu $K\alpha$)= 5.80 cm^{-1}.

Integrated intensities were measured on the diffractometer by the θ—2θ scan technique. The 2θ scan rate and scan width were 4° min^{-1} and $\Delta 2\theta$=(2.0+0.7 tanθ)°, respectively. Backgrounds were measured for 7.5 s before and after the scan of each peak. Intensities of five standard reflections were measured after every 52 reflections, $|F|$ values of which changed about 3 to 5% with time. Their changes could be expressed approximately by a fifth order equation, the coefficients of which were determined from the intensity changes of three stronger reflections, 080, 0,0,16, and 600, and the observed $|F|$ values were corrected with time. A total of 6993 independent (5215 non-zero) reflections was collected up to 2θ=110°. Usual Lorentz and polarization corrections were made but absorption and extinction corrections were ignored.

Solution of the Structure and Refinement

The crystal data show that the corresponding space group is Pbca and 40 molecules are contained per unit cell. The asymmetric unit consists of 5 independent molecules.

The structure could be established by the direct method using *MULTAN* program.[4] Of the 32 choices of the starting sets, only one gave the figure of merit larger than 0.8. The $|E|$ map was then computed using the phases based on this starting set. 54 peaks out of 75 high peaks in the $|E|$ map revealed non-hydrogen atoms of three independent molecules out of five and also parts of the ethyl and carbazole moieties of the other molecules. The successive Fourier synthesis could locate all of the remaining non-hydrogen atoms.

The structure was refined anisotropically by the block-diagonal least-squares procedure (*HBLS* V).[5] The function minimized was $\sum w(\Delta F)^2$, where w=1. Hydrogen atoms except those of the methyl groups were located on a difference Fourier map, which were refined isotropically. In the final cycle of the refinement the R index decreased to 0.062 for 5134 non-zero reflections. Final atomic coordinates with equivalent temperature factors[6] are listed in Table 1.††††

Atomic scattering factors for non-hydrogen atoms were taken from International Tables for X-Ray Crystallography, Vol. IV,[7] and those of hydrogen atoms from Stewart and co-workers.[8]

All the Computations were carried out mainly on a NEAC 2200-700 computer at the Computation Center and at the final stage on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Molecular Structure. Since five independent molecules do not differ significantly from each other, only the structure of the molecule 1 is depicted in Fig. 1, with the numbering scheme of atoms. Bond lengths and bond angles in five molecules are given in Table 2.†††††

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††††Tables of anisotropic thermal parameters, atomic coordinates of hydrogen atoms and observed and calculated structure factors are deposited at the Chemical Society of Japan, Document No. 8533.

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TABLE 1. FINAL ATOMIC COORDINATES OF *N*-ETHYLCARBAZOLE WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

a) Non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å²	Atom	*x*	*y*	*z*	B_{eq}/Å²
N(100)	0.3233(4)	0.41703(13)	0.13319(6)	4.6	C(312)	0.1145(6)	0.28523(17)	0.05090(7)	5.0
C(101)	0.4112(5)	0.40700(16)	0.11243(7)	4.4	C(313)	−0.0027(7)	0.32490(17)	0.04540(8)	5.9
C(102)	0.3807(6)	0.36841(18)	0.09521(8)	5.9	C(314)	−0.1279(6)	0.31603(18)	0.02891(8)	5.9
C(103)	0.4872(7)	0.36735(21)	0.07609(9)	7.6	C(315)	−0.1409(5)	0.26683(17)	0.01753(7)	4.9
C(104)	0.6184(7)	0.40381(22)	0.07409(9)	7.0	C(316)	−0.0245(5)	0.22619(15)	0.02259(6)	3.7
C(105)	0.6504(6)	0.44167(18)	0.09127(8)	5.3	C(370)	0.3517(6)	0.18566(18)	0.05579(8)	5.3
C(106)	0.5450(5)	0.44390(16)	0.11072(7)	4.0	C(380)	0.5039(6)	0.20720(21)	0.04334(9)	7.0
C(111)	0.3944(5)	0.46114(16)	0.14424(7)	4.3	N(400)	−0.0242(5)	0.44367(15)	0.20091(6)	5.6
C(112)	0.3469(6)	0.48760(17)	0.16492(7)	5.2	C(401)	0.0721(5)	0.40287(18)	0.21029(7)	4.8
C(113)	0.4382(6)	0.53245(18)	0.17170(8)	5.8	C(402)	0.0558(7)	0.34685(20)	0.20761(8)	6.3
C(114)	0.5768(6)	0.55029(17)	0.15914(8)	5.6	C(403)	0.1684(8)	0.31417(21)	0.21931(9)	7.7
C(115)	0.6272(6)	0.52346(16)	0.13882(7)	4.9	C(404)	0.2951(7)	0.33545(23)	0.23331(9)	7.8
C(116)	0.5353(5)	0.47853(15)	0.13123(7)	3.9	C(405)	0.3112(6)	0.39060(22)	0.23612(7)	6.4
C(170)	0.1583(6)	0.39463(18)	0.13926(8)	5.5	C(406)	0.1992(5)	0.42500(18)	0.22457(7)	5.0
C(180)	0.0152(6)	0.42576(20)	0.12829(10)	7.0	C(411)	0.0339(6)	0.49224(18)	0.20955(7)	5.4
N(200)	0.1800(4)	0.09878(14)	0.42261(6)	5.0	C(412)	−0.0257(7)	0.54428(21)	0.20522(10)	7.7
C(201)	0.0986(5)	0.05792(17)	0.43441(7)	4.9	C(413)	0.0560(9)	0.58659(22)	0.21578(11)	9.5
C(202)	0.1362(6)	0.03274(21)	0.45601(8)	6.9	C(414)	0.1947(9)	0.57813(23)	0.23034(10)	9.5
C(203)	0.0294(8)	−0.00807(23)	0.46361(9)	8.0	C(415)	0.2560(7)	0.52651(22)	0.23458(8)	7.4
C(204)	−0.1070(7)	−0.02505(20)	0.45036(9)	7.3	C(416)	0.1743(6)	0.48251(19)	0.22411(7)	5.4
C(205)	−0.1436(6)	−0.00093(17)	0.42926(8)	5.8	C(470)	−0.1822(6)	0.43554(21)	0.18842(8)	6.7
C(206)	−0.0404(5)	0.04091(16)	0.42092(7)	4.5	C(480)	−0.3300(6)	0.43108(23)	0.20520(9)	7.3
C(211)	0.0995(5)	0.10749(16)	0.40137(7)	4.5	N(500)	0.1906(5)	0.28059(14)	0.33122(7)	5.8
C(212)	0.1407(6)	0.14301(17)	0.38320(8)	5.6	C(501)	0.2851(6)	0.27188(17)	0.35128(8)	5.7
C(213)	0.0422(7)	0.14239(19)	0.36337(9)	6.4	C(502)	0.2694(7)	0.29519(19)	0.37376(9)	6.7
C(214)	−0.0966(6)	0.10866(19)	0.36132(8)	6.2	C(503)	0.3828(8)	0.27928(22)	0.39068(9)	8.0
C(215)	−0.1388(6)	0.07398(17)	0.37948(8)	5.2	C(504)	0.5081(7)	0.24275(22)	0.38622(9)	7.8
C(216)	−0.0394(5)	0.07277(15)	0.39981(7)	4.1	C(505)	0.5254(6)	0.21951(20)	0.36415(9)	6.9
C(270)	0.3410(6)	0.12253(21)	0.42920(9)	6.5	C(506)	0.4123(6)	0.23432(17)	0.34629(8)	5.4
C(280)	0.4873(6)	0.09255(23)	0.41845(10)	7.8	C(511)	0.2499(6)	0.24685(17)	0.31357(8)	5.5
N(300)	0.2000(4)	0.18948(12)	0.04151(6)	4.2	C(512)	0.1910(7)	0.24082(20)	0.29050(9)	7.0
C(301)	0.1394(5)	0.15101(15)	0.02581(7)	4.1	C(513)	0.2737(8)	0.20527(23)	0.27600(9)	8.3
C(302)	0.2002(6)	0.09864(17)	0.02182(8)	5.3	C(514)	0.4115(8)	0.17573(21)	0.28425(10)	8.3
C(303)	0.1169(7)	0.06783(17)	0.00532(9)	6.5	C(515)	0.4715(7)	0.18157(19)	0.30681(9)	6.8
C(304)	−0.0203(7)	0.08780(19)	−0.00673(8)	6.5	C(516)	0.3889(6)	0.21767(17)	0.32199(8)	5.5
C(305)	−0.0820(6)	0.13942(18)	−0.00282(8)	5.5	C(570)	0.0314(7)	0.31002(20)	0.33027(9)	7.1
C(306)	−0.0003(5)	0.17197(15)	0.01385(6)	3.9	C(580)	−0.1157(7)	0.27405(23)	0.33681(11)	8.7
C(311)	0.1015(5)	0.23559(15)	0.03932(6)	3.7					

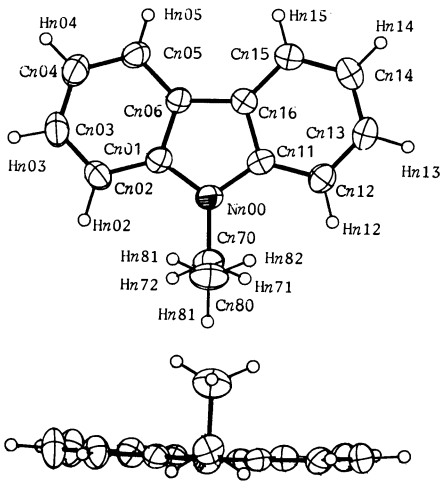
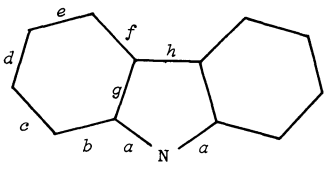


Fig. 1. Molecular structure of *N*-ethylcarbazole (*ORTEP* drawing).[11]
Non-hydrogen atoms are drawn as thermal ellipsoids with 30% probability level and hydrogen atoms as spheres with $B=1.0$ Å².
(a) Plan. (b) Side view.

The carbazole moiety is approximately planar (Fig. 1(b)), and no significant difference has been observed between chemically-equivalent bond lengths and bond angles. Average values of bond lengths and bond angles are compared in Table 3 with those of carbazole[9] and *N*-vinylcarbazole.[10] All of the corresponding lengths and angles in the three compounds show accordances within the limit of errors.

In each of the present *N*-ethylcarbazole molecule, the C(*n*01)-N(*n*00)-C(*n*70) angle [av. 125.3°] is equal to the corresponding C(*n*11)-N(*n*00)-C(*n*70) angle [av. 124.5°] and the N(*n*00)-C(*n*01)-C(*n*02) [av. 129.7°] equal to the N(*n*00)-C(*n*11)-C(*n*12) [av. 129.8°]. The ethyl group attached to the nitrogen atom is almost perpendicular to the carbazole plane [av. 87.8°]. On the other hand, in *N*-vinylcarbazole the ethylenic bond planes in two independent molecules make angles of 14.0 and 2.6° with the carbazole planes. The C(01)-N-C(70) angle [128.6(7) or 130.6(7)°] is, therefore, much larger than the C(11)-N-C(70) angle[122.9(7) or

TABLE 3. COMPARISON OF AVERAGE BOND LENGTH AND BOND ANGLES IN CARBAZOLE RING



	N-Ethyl-carbazole[a]	*N*-Vinyl-carbazole[10]	Carbazole[9]
Bond lengths[*l*/Å][b]			
a	1.372(8)	1.393(2)	1.394
b	1.391(6)	1.404(7)	1.404
c	1.365(6)	1.378(8)	1.374
d	1.367(8)	1.389(8)	1.394
e	1.374(6)	1.385(7)	1.392
f	1.385(6)	1.388(2)	1.391
g	1.386(4)	1.401(3)	1.408
h	1.437(9)	1.442(7)	1.479
Bond angles[ϕ/°][b]			
aa	109.0(2)	108.3(1)	108.4
ab	129.8(3)	129.6(4)	128.4
ag	108.8(2)	109.0(4)	109.7
bg	121.5(2)	121.5(6)	121.9
bc	118.1(1)	117.0(5)	115.6
cd	121.2(2)	122.1(7)	123.9
de	121.1(2)	120.8(8)	120.1
ef	119.3(2)	118.6(9)	117.9
fh	134.4(2)	133.0(6)	133.3
fg	118.8(1)	120.1(9)	120.6
gh	106.7(2)	106.9(4)	106.1

a) Present study. b) Average: $\bar{x}=\sum x_i/n$, where x_i is the individual bond length or angle observed, and n is the number of chemically equivalent structural parameters. Estimated standard deviation of average: $\sigma(\bar{x})=\{\sum (x_i-\bar{x})^2/n(n-1)\}^{1/2}$

TABLE 4. INTERMOLECULAR ATOMIC CONTACTS LESS THAN 3.6 Å[*l*/Å]

C(270)···C(301)[a]	3.518(6)	C(105)···C(180)[b]	3.552(7)
C(370)···N(200)[a]	3.551(5)	C(380)···C(315)[b]	3.457(7)
C(380)···N(200)[a]	3.566(6)	C(380)···C(480)[b]	3.445(8)
		C(505)···C(580)[b]	3.466(8)

key, a: 0.5+*x*, *y*, 0.5−*z*,
b: 1+*x*, *y*, *z*.

121.2(7)°].[10] The carbazole molecule has crystallographic mirror symmetry about the plane, vertical to the C(06)–C(16), which includes the N and H atoms.[9]

Crystal Structure. Figure 2 shows the crystal structure of *N*-ethylcarbazole projected along the a axis. Carbazole rings of the five independent molecules make similar angles with the a axis, the angles ranging from 36.1 to 38.3°. It is remarkable that no pair of neighboring molecules, in which the π-electron clouds of the carbazole rings overlaps, is found. All the molecules contact with each other by the van der Waals force (Table 4). The closest intermolecular distance between non-hydrogen atoms is observed between molecules directly related by the glide plane [C(405)(*x*, *y*, *z*)···C(480)(1+*x*, *y*, *z*)=3.445(8) Å]. In

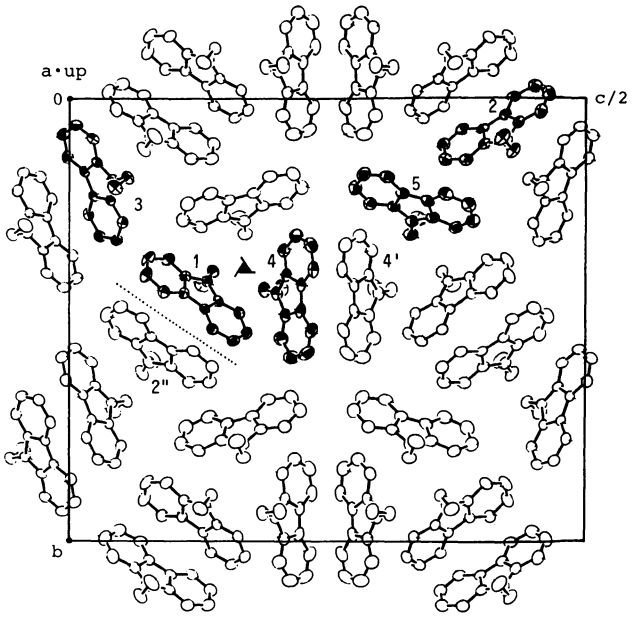


Fig. 2. Crystal structure of *N*-ethylcarbazole (*ORTEP* drawing).[11]
Non-hydrogen atoms are drawn as thermal ellipsoids with 30% probability level. Hydrogen atoms are omitted for clarity. Atoms belong to the five molecules in an asymmetric unit are drawn as ellipsoids with principal and enveloping ellipses whereas others only with enveloping ellipses.
Local pseudo symmetries are also given.

the packing of molecules the following pseudo-symmetries can be locally observed besides the crystallographic symmetry operations: 1) a local pseudo a-glide plane, expressed by a broken line in Fig. 2, between the molecules 1 (*x*, *y*, *z*) and 2″ (−*x*, 0.5+*y*, 0.5−*z*) and 2) a local pseudo three-fold screw axis parallel to the a axis among the molecules 4 (*x*, *y*, *z*), 1 (*x*, *y*, *z*), and 5 (0.5+*x*, *y*, 0.5−*z*).

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References

1) K. Kato, M. Yokoyama, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **47**, 1795 (1974); K. Kato, T. Nogami, M. Yokoyama, and H. Mikawa, *Chem. Lett.*, **1974**, 1097.

2) M. Yokoyama, S. Shimokihara, A. Matsubara, and H. Mikawa, *J. Chem. Phys.*, **76**, 724 (1982).

3) K. Kato, M. Yokoyama, K. Okamoto, S. Kusabayashi, H. Mikawa, K. Yoshihara and S. Nagakura, *Mol. Cryst. Liq. Cryst.*, **28**, 37 (1974).

4) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

5) T. Ashida, *HBLS* V, "The Universal crystallographic Computing System-Osaka," The Computation Center, Osaka Univ., 1973, p. 55.

6) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).
7) International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974), p. 71.
8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
9) M. Kurahashi, M Fukuyo, A. Shimada, A. Furusaki, I. Nitta, *Bull. Chem. Soc. Jpn.*, **42**, 2174 (1969).
10) K. Tsutsui, K. Hirotsu, M. Umesaki, M. Kurahashi, A. Shimada, T. Higuchi, *Acta Crystallogr., Sect. B*, **32**, 3049 (1976).
11) C. K. Johnson, *ORTEP* II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976).