

Structural Chemistry of Polymerizable Monomers. I. Crystal Structure of *N*-Vinylcarbazole

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The crystal structure of *N*-vinylcarbazole was determined from diffractometer data collected at room temperature: orthorhombic, space group $Pna2_1$, $a = 21.602$ (6), $b = 17.232$ (6), $c = 5.558$ (2) Å and $Z = 8$. The structure was solved by direct methods and refined by block-diagonal least squares to an R of 0.053 for 908 reflexions. There are two independent molecules in the asymmetric unit; each is almost planar and separately stacked along the c axis. The nearest neighbouring vinyl groups are between these two stackings.

Introduction

Under γ -irradiation some vinyl monomers polymerize in the solid state (Magat, 1962; Morawetz, 1963; Bamford & Eastmond, 1969; Chatani, 1974). In the solid-state polymerization, monomer crystal structure is expected to play an important role in determining the chain growth direction (Restaino, Mesrobian, Morawetz, Ballantine, Dienes & Metz, 1956; Hirshfeld & Schmidt, 1964; Morawetz, 1966; Chatani, 1974). *N*-Vinylcarbazole (NVC) is of great interest in the field of solid-state polymerization (*Encyclopedia of Polymer Science and Technology*, 1971). Gałdecki, Karolak, Pekala & Kroh (1967) proposed an arrangement of molecules and a chain growth direction in the NVC crystal on the basis of the microscopy of fibrous polymer aggregates and the unit-cell dimensions. This paper deals with the crystal analysis of monomeric NVC and then discusses the correlation between its crystal structure and its reaction in solid-state polymerization.

Experimental

Crystals of colourless plates obtained from a methanol solution belong to the orthorhombic system. The systematic absences $h0l$ with h odd, and $0kl$ with $k+l$ odd suggest that the space group is either $Pna2_1$ or $Pnam$. $Pna2_1$ was adopted after the result of a piezoelectric test (Gałdecki, Karolak, Pekala & Kroh, 1967) and molecular packing with a short c axis were considered. The unit-cell dimensions were obtained from the least-squares refinement of reflexions measured on a Philips PW1100 four-circle diffractometer. Crystal data are given in Table 1. There are two independent molecules in the asymmetric unit. The crystal selected for X-ray intensity measurement with Mo $K\alpha$ radiation was ap-

proximately $0.41 \times 0.44 \times 0.25$ mm. The intensities of 1613 independent reflexions (up to $\theta = 23.0^\circ$) were measured with the ω scan technique, a scan rate of $3.6^\circ \text{ min}^{-1}$ and scan width of $1.0^\circ + 0.3^\circ \tan \theta$. The intensities of the three standard reflexions were recorded every 2h to monitor the crystal stability and its alignment. These reflexions exhibited about 3.8% reduction in intensity during data collection. The data were corrected for Lorentz and polarization effects, but not for absorption. Intensities were converted to normalized structure amplitudes ($|E|$) with a temperature factor (B) of 5.5 \AA^2 .

Table 1. Crystal data

<i>N</i> -Vinylcarbazole, $C_{14}H_{11}N$	
Molecular weight 193.25	
Orthorhombic	
Space group $Pna2_1$	
$a = 21.602$ (6) Å	$D_m = 1.17 \text{ g cm}^{-3}$
$b = 17.232$ (6)	$D_x = 1.241$
$c = 5.558$ (2)	$\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$
$Z = 8$	$\mu(\text{Mo } K\alpha) = 1.57 \text{ cm}^{-1}$

Determination and refinement of the structure

The crystal structure was solved by direct methods. Multi-tangent refinements (Germain, Main & Woolfson, 1971) were applied to 377 reflexions with $|E| > 1.2$. Three of the 32 phase combinations were consistent sets; $R = 0.26, 0.27$ and 0.27 . An E map calculated with phases from the first set gave the positions of 27 non-hydrogen atoms. The three remaining C atoms were found by difference Fourier synthesis. The difference Fourier map followed by anisotropic block-diagonal least-squares refinements with unit weights revealed all the H atoms. Further refinements were carried out using the following weighting scheme: $w = 0.05$ for $F_o < F_{\min}$; $w = 1.0$ for $F_{\min} \leq F_o \leq F_{\max}$; $w = (F_{\max}/F_o)^2$ for $F_o > F_{\max}$.

The final R value was 0.053 for the 908 reflexions where $I > 2\sigma(I)$. Scattering factors for C and N were from *International Tables for X-ray Crystallography*

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(1974). The curve for H was that of Stewart, Davidson & Simpson (1965). The final positional and thermal parameters are shown in Table 2.*

Results and discussion

Fig. 1 shows the geometry of two independent molecules, (I) and (II), with the atomic numbering. Bond distances and angles are given in Table 3. The carbazole moiety exhibits no significant differences between chemically-equivalent bonds. Mean values of bond distances and angles are compared with those of carba-

zole (Kurahashi, Fukuyo & Shimada, 1969), which has crystallographic mirror symmetry (Table 4). In each of the molecules the exocyclic angles on both sides of the N atoms are different; C(1)-N-C(13) 128.6 (7), C(12)-N-C(13) 122.9 (7), C(1')-N'-C(13') 130.6 (7) and C(12')-N'-C(13') 121.2 (7)°. These differences may be ascribed to non-bonded repulsions of H(1)···H(11), 1.67, and H(1')···H(11'), 1.67 Å. The lengths of both ethylenic C=C bonds, 1.29 (1) and 1.23 (2) Å, are seemingly shorter than usual; this is because of the large thermal motion of the exocyclic C atoms.

Table 5 shows the deviations of atoms from the least-squares planes through the carbazole skeletons. Both carbazole skeletons (I) and (II) are planar within 0.05 and 0.04 Å respectively. Carbazole plane (I) is inclined to the (001) plane at 52.5 and (II) at 53.6°. Both C(13) and C(13') of the vinyl groups are coplanar with car-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31906 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional* ($\times 10^4$ for non-H atoms and $\times 10^3$ for H atoms) and thermal parameters ($\times 10^4$ for non-H atoms)

Standard deviations are in parentheses. The values of anisotropic thermal parameters β_{ij} are defined by the expression:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	966 (3)	2995 (4)	2829 (13)	24 (2)	40 (3)	431 (30)	1 (4)	-15 (15)	-33 (18)
C(1)	659 (4)	3344 (4)	920 (16)	23 (2)	38 (3)	417 (38)	7 (5)	33 (18)	-21 (22)
C(2)	672 (4)	4124 (5)	123 (17)	28 (2)	48 (4)	437 (40)	11 (5)	-23 (18)	-33 (22)
C(3)	307 (4)	4297 (5)	-1804 (19)	39 (3)	52 (4)	588 (53)	8 (6)	-57 (24)	72 (28)
C(4)	-65 (4)	3764 (6)	-2954 (20)	28 (3)	75 (5)	571 (51)	11 (6)	-60 (20)	32 (29)
C(5)	-80 (4)	2997 (5)	-2161 (17)	29 (2)	62 (4)	428 (39)	5 (6)	-52 (20)	2 (24)
C(6)	278 (4)	2787 (4)	-195 (16)	23 (2)	41 (3)	349 (33)	1 (4)	0 (16)	-2 (19)
C(7)	358 (4)	2078 (4)	1085 (17)	22 (2)	42 (3)	420 (35)	-15 (4)	25 (18)	-85 (22)
C(8)	107 (4)	1339 (5)	886 (18)	24 (2)	54 (4)	493 (43)	-7 (5)	13 (20)	-66 (25)
C(9)	277 (4)	769 (5)	2465 (19)	35 (3)	40 (4)	596 (47)	-1 (5)	66 (22)	-41 (25)
C(10)	688 (4)	923 (5)	4356 (22)	33 (3)	45 (4)	612 (48)	5 (6)	34 (23)	46 (27)
C(11)	950 (4)	1653 (5)	4615 (18)	31 (2)	45 (4)	400 (35)	3 (5)	12 (20)	-10 (24)
C(12)	776 (4)	2218 (4)	2959 (17)	27 (2)	28 (3)	494 (41)	-7 (4)	36 (19)	-41 (21)
C(13)	1432 (4)	3303 (5)	4293 (20)	40 (3)	49 (4)	450 (42)	-7 (6)	-60 (22)	-8 (26)
C(14)	1743 (5)	3935 (6)	4060 (25)	46 (3)	58 (5)	830 (65)	-9 (7)	-215 (28)	48 (34)
N'	3279 (3)	1912 (4)	4604 (16)	31 (2)	48 (3)	378 (27)	15 (4)	24 (16)	33 (19)
C(1')	2845 (4)	1546 (5)	6070 (17)	24 (2)	51 (4)	372 (34)	5 (5)	-21 (18)	38 (23)
C(2')	2623 (4)	788 (5)	5964 (20)	35 (3)	49 (4)	568 (46)	-1 (6)	-3 (23)	42 (27)
C(3')	2200 (5)	574 (5)	7743 (20)	39 (3)	42 (4)	699 (53)	-7 (6)	-18 (25)	48 (28)
C(4')	1986 (4)	1094 (5)	9496 (20)	34 (3)	61 (5)	525 (45)	-3 (6)	62 (23)	101 (28)
C(5')	2221 (4)	1842 (5)	9556 (19)	26 (2)	57 (4)	406 (35)	3 (5)	-9 (19)	28 (24)
C(6')	2643 (4)	2071 (5)	7825 (16)	25 (2)	46 (4)	358 (34)	9 (5)	-7 (18)	51 (20)
C(7')	2975 (4)	2796 (4)	7415 (16)	23 (7)	46 (4)	372 (36)	4 (5)	-7 (17)	8 (22)
C(8')	2978 (4)	3495 (5)	8669 (19)	35 (3)	51 (4)	545 (47)	18 (6)	22 (22)	-27 (25)
C(9')	3359 (4)	4076 (5)	7750 (22)	37 (3)	42 (4)	729 (56)	-8 (6)	-80 (26)	-19 (28)
C(10')	3730 (4)	3965 (5)	5768 (22)	33 (3)	50 (4)	702 (58)	-7 (5)	-46 (24)	63 (29)
C(11')	3730 (4)	3278 (5)	4539 (22)	29 (2)	57 (4)	546 (44)	14 (5)	-36 (22)	47 (28)
C(12')	3349 (4)	2670 (5)	5402 (15)	28 (2)	47 (4)	412 (40)	14 (5)	23 (18)	97 (21)
C(13')	3630 (5)	1624 (6)	2659 (19)	44 (3)	59 (5)	483 (44)	23 (7)	11 (24)	44 (28)
C(14')	3638 (6)	973 (6)	1736 (25)	60 (4)	62 (5)	730 (63)	34 (8)	0 (29)	-46 (31)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	99 (3)	450 (4)	104 (14)	6.52 (1)	H(1')	281 (3)	40 (4)	436 (18)	7.37 (1)
H(2)	33 (3)	486 (4)	-256 (14)	5.84 (1)	H(2')	201 (3)	3 (4)	771 (14)	5.69 (1)
H(3)	-36 (3)	383 (4)	-442 (14)	7.28 (1)	H(3')	175 (3)	94 (4)	1098 (15)	6.57 (1)
H(4)	-37 (3)	259 (4)	-288 (14)	6.49 (1)	H(4')	209 (3)	223 (4)	1103 (15)	7.22 (1)
H(5)	-18 (3)	121 (4)	-51 (15)	5.73 (1)	H(5')	268 (3)	366 (4)	986 (14)	6.01 (1)
H(6)	10 (4)	17 (4)	236 (15)	6.94 (1)	H(6')	337 (3)	458 (4)	872 (15)	6.32 (1)
H(7)	80 (3)	43 (4)	517 (15)	7.94 (1)	H(7')	404 (3)	442 (4)	521 (15)	7.48 (1)
H(8)	127 (3)	176 (4)	588 (15)	6.65 (1)	H(8')	399 (3)	308 (4)	319 (14)	6.83 (1)
H(9)	150 (4)	304 (4)	584 (15)	7.56 (1)	H(9')	387 (4)	196 (4)	165 (17)	7.46 (1)
H(10)	201 (3)	397 (4)	556 (14)	7.67 (1)	H(10')	394 (4)	71 (5)	25 (16)	9.07 (1)
H(11)	160 (4)	438 (4)	283 (16)	8.62 (1)	H(11')	340 (4)	48 (4)	247 (17)	8.35 (1)

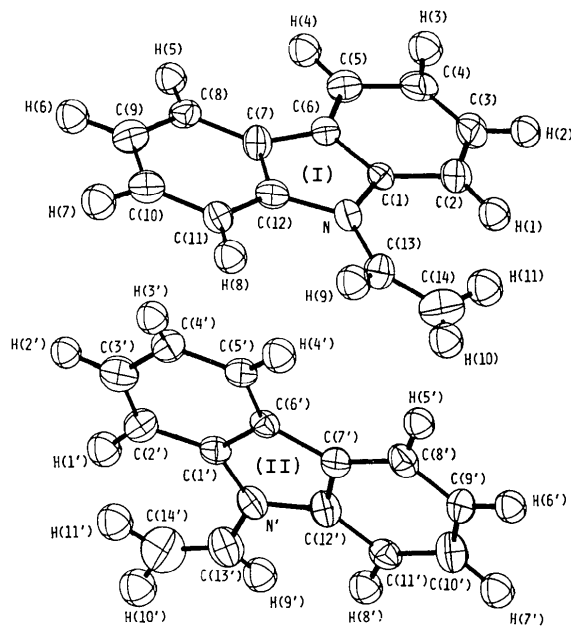


Fig. 1. Molecular structure illustrating the thermal ellipsoids with a probability of 0.20, and the numbering system.

bazole planes. Thus orbitals of atoms N and N' are mainly sp^2 type. The ethylenic-bond planes make angles of 14.0 and 2.6° with planes (I) and (II) respectively.

Fig. 2 shows the crystal structure of NVC. Two kinds of flat molecules are stacked separately along

Table 3. Bond distances and angles

(a) Bond distances (Å)

N—C(1)	1.388 (11)	N'—C(1')	1.393 (11)
N—C(12)	1.403 (9)	N'—C(12')	1.388 (10)
N—C(13)	1.398 (12)	N'—C(13')	1.411 (13)
C(1)—C(2)	1.414 (11)	C(1')—C(2')	1.393 (12)
C(1)—C(6)	1.409 (11)	C(1')—C(6')	1.399 (12)
C(2)—C(3)	1.363 (13)	C(2')—C(3')	1.396 (14)
C(3)—C(4)	1.377 (13)	C(3')—C(4')	1.402 (14)
C(4)—C(5)	1.393 (13)	C(4')—C(5')	1.387 (12)
C(5)—C(6)	1.386 (12)	C(5')—C(6')	1.383 (12)
C(6)—C(7)	1.425 (11)	C(6')—C(7')	1.459 (11)
C(7)—C(8)	1.389 (11)	C(7')—C(8')	1.392 (13)
C(7)—C(12)	1.399 (12)	C(7')—C(12')	1.396 (12)
C(8)—C(9)	1.367 (13)	C(8')—C(9')	1.392 (13)
C(9)—C(10)	1.401 (14)	C(9')—C(10')	1.376 (15)
C(10)—C(11)	1.386 (11)	C(10')—C(11')	1.366 (14)
C(11)—C(12)	1.391 (12)	C(11')—C(12')	1.416 (12)
C(13)—C(14)	1.287 (13)	C(13')—C(14')	1.233 (15)

Table 3 (cont.)

(b) Bond angles (°)

C(1)—N—C(12)	108.3 (7)	C(7)—C(8)—C(9)	120.1 (8)	C(3')—C(4')—C(5')	119.3 (9)
C(1)—N—C(13)	128.6 (7)	C(8)—C(9)—C(10)	121.1 (8)	C(4')—C(5')—C(6')	119.3 (9)
C(12)—N—C(13)	122.9 (7)	C(9)—C(10)—C(11)	120.5 (9)	C(1')—C(6')—C(5')	120.4 (8)
N—C(1)—C(2)	129.9 (7)	C(10)—C(11)—C(12)	117.2 (9)	C(1')—C(6')—C(7')	106.9 (7)
N—C(1)—C(6)	108.7 (7)	N—C(12)—C(7)	108.3 (7)	C(5')—C(6')—C(7')	132.6 (8)
C(2)—C(1)—C(6)	121.4 (8)	N—C(12)—C(11)	128.6 (8)	C(6')—C(7')—C(8')	131.7 (8)
C(1)—C(2)—C(3)	116.3 (8)	C(7)—C(12)—C(11)	123.1 (7)	C(6')—C(7')—C(12')	106.1 (7)
C(2)—C(3)—C(4)	123.8 (9)	N—C(13)—C(14)	129.7 (10)	C(8')—C(7')—C(12')	122.2 (8)
C(3)—C(4)—C(5)	120.0 (9)	C(1')—N'—C(12')	108.2 (7)	C(7')—C(8')—C(9')	116.1 (9)
C(4)—C(5)—C(6)	118.9 (8)	C(1')—N'—C(13')	130.6 (7)	C(8')—C(9')—C(10')	122.6 (9)
C(1)—C(6)—C(5)	119.7 (7)	C(12')—N'—C(13')	121.2 (7)	C(9')—C(10')—C(11')	121.4 (9)
C(1)—C(6)—C(7)	107.1 (7)	N'—C(1')—C(2')	129.2 (9)	C(10')—C(11')—C(12')	118.1 (10)
C(5)—C(6)—C(7)	133.3 (8)	N'—C(1')—C(6')	109.0 (7)	N'—C(12')—C(7')	109.8 (7)
C(6)—C(7)—C(8)	134.4 (8)	C(2')—C(1')—C(6')	121.9 (8)	N'—C(12')—C(11')	130.6 (8)
C(6)—C(7)—C(12)	107.6 (7)	C(1')—C(2')—C(3')	116.3 (9)	C(7')—C(12')—C(11')	119.6 (8)
C(8)—C(7)—C(12)	118.0 (8)	C(2')—C(3')—C(4')	122.7 (8)	N'—C(13')—C(14')	130.3 (10)

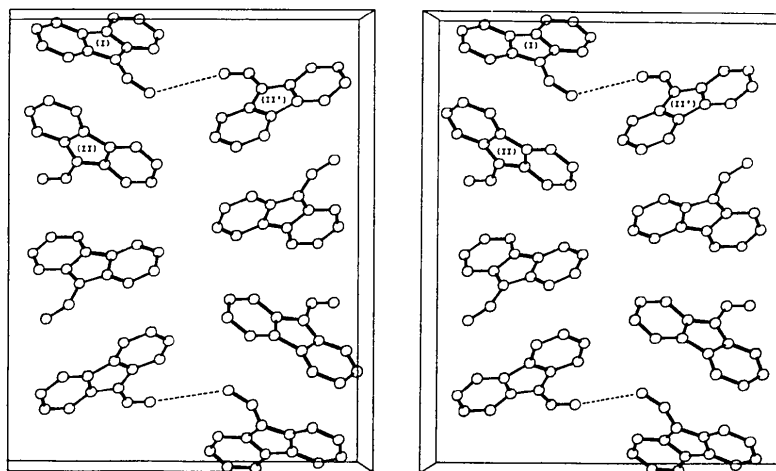
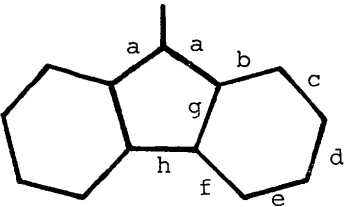


Fig. 2. Stereoscopic view of the crystal structure of NVC looking along the c axis. The broken lines indicate the closest contacts between vinyl groups.

Table 4. Comparison of bond distances and angles



	NVC	Carbazole	NVC	Carbazole
<i>a</i>	1.393 Å	1.394 Å	<i>aa</i>	108.3°
<i>b</i>	1.404	1.404	<i>ab</i>	129.6
<i>c</i>	1.378	1.374	<i>ag</i>	109.0
<i>d</i>	1.389	1.394	<i>bg</i>	121.5
<i>e</i>	1.385	1.392	<i>bc</i>	117.0
<i>f</i>	1.388	1.391	<i>cd</i>	122.1
<i>g</i>	1.401	1.408	<i>de</i>	120.8
<i>h</i>	1.442	1.479	<i>ef</i>	118.6
			<i>fh</i>	133.0
			<i>fg</i>	120.1
			<i>gh</i>	106.9
				106.1

Table 5. Least-squares planes and deviations (Å)

Plane (I): $-0.753X + 0.250Y + 0.608Z = 0.709$ Plane (II): $0.742X - 0.311Y + 0.594Z = 5.740$

Atoms not included in the plane calculations are indicated by an asterisk.

	(I)	(II)	
N	-0.03	N'	0.01
C(1)	-0.03	C(1')	0.00
C(2)	0.02	C(2')	0.01
C(3)	0.04	C(3')	0.03
C(4)	0.02	C(4')	-0.01
C(5)	-0.02	C(5')	-0.01
C(6)	-0.02	C(6')	-0.03
C(7)	-0.03	C(7')	-0.02
C(8)	-0.01	C(8')	0.02
C(9)	0.01	C(9')	0.02
C(10)	0.04	C(10')	0.02
C(11)	0.02	C(11')	-0.02
C(12)	-0.01	C(12')	-0.02
C(13)*	-0.16	C(13')*	0.09
C(14)*	-0.48	C(14')*	0.14

Table 6. Pertinent intermolecular distances for non-hydrogen atoms

Atom in (x, y, z)	to atom	in unit	Distance
C(11)	C(4')	1	3.65 (2) Å
N	C(4)	2	3.49 (1)
N	C(5)	2	3.59 (1)
C(11)	C(5)	2	3.68 (2)
C(12)	C(5)	2	3.55 (2)
C(13)	C(3)	2	3.68 (2)
C(13)	C(4)	2	3.66 (2)
C(5')	N'	2	3.62 (1)
C(5')	C(13')	2	3.52 (2)
C(5')	C(14')	2	3.62 (2)
C(6')	C(13')	2	3.51 (2)
C(6')	C(14')	2	3.59 (2)
C(8')	C(11')	2	3.66 (2)
C(11')	C(8)	3	3.66 (2)

Unit code: (1) x, y, z . (2) $x, y, 1+z$. (3) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

the *c* axis at the above-mentioned angles to the (001) plane. The interplanar distance is 3.38 Å for stacking (I) and 3.30 Å for stacking (II). All intermolecular distances up to 3.7 Å are listed in Table 6.

The closest contact (Fig. 2) between the vinyl groups is between stackings (I) and (II'); the centre-to-centre distance is 4.94 Å, and the head-to-head distance is 3.90 Å. This contact is further illustrated in Fig. 3. The two vinyl groups of molecules (I) and (II') make a dihedral angle of 140.3°. The symbols *H* and *T* in this figure refer to the head (CH₂=) and tail (=) respectively of the vinyl group. On the other hand, the centres of the vinyl groups of molecules (I) and (II) are 6.06 Å apart. Other intercentric spacings between vinyl groups are more than 5.5 Å. The present shortest centre-to-centre spacing (4.94 Å) is much longer than those of the α class (3.6–4.1) and β class (3.9–4.1 Å) of cinnamic acid derivatives which photodimerize or isomerize in the solid state. However, the interatomic distance $H \cdots H$ 3.90 Å is similar to those ($T \cdots T$ 3.83, $H \cdots H$ 3.85, $T \cdots T$ 3.68 Å) in the photopolymerizable monomer crystals of acrylic acid (Chatani, Sakata & Nitta, 1963; Higgs & Sass, 1963) and acrylamide (Isakov, 1966; Nitta, Taguchi & Chatani, 1959; Chatani, 1974). Although the vinyl groups in the NVC crystal are arranged unfavourably for solid-state polymerization, the reaction proceeds by high-energy radiation. Since the melting point of this compound is not very high (65°C), the almost flat molecules may be easily moved in the lattice by radiation or warming, and then the olefinic π orbitals between adjacent molecules of NVC may overlap each other through the process of reaction. That is, the initial polymerization step seems to begin preferentially between stackings (I) and (II') along the *b* axis.

All calculations were performed on the FACOM 270/30 computer at the Computer Centre of Osaka City University with the following programs: *RSSFR-3* and *HBL-IV* in *UNICS* (1967) and *DEAM*

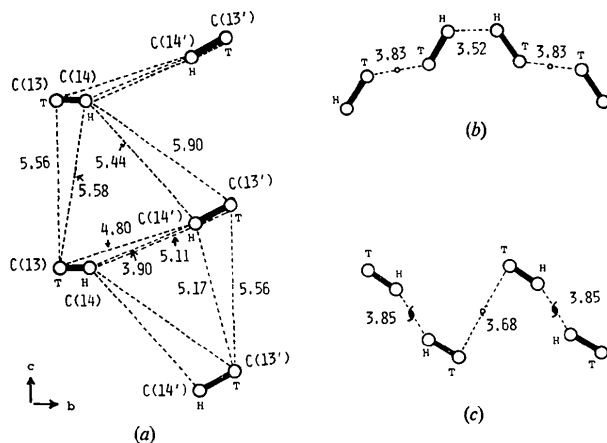


Fig. 3. The geometry of contacts between neighbouring $>C=CH_2$ groups. (a) *N*-Vinylcarbazole. (b) Acrylic acid. (c) Acrylamide.

(Takenaka, 1972). Programs for tangent refinement (*PHASE-III*) written by one of the authors (K.H.), bond dimensions (*BOND*) by Mr H. Yoshioka and stereoscopic drawing (*TECS*) by Dr F. Takusagawa were also used.

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The Crystal and Molecular Structure of the Bromolactone of Echinocystic Acid Diacetate, $C_{34}H_{51}O_6Br$

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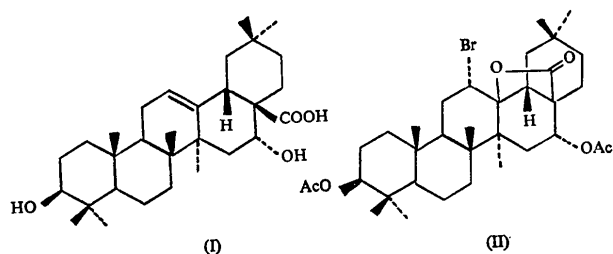
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The bromolactone of echinocystic acid diacetate crystallizes in the monoclinic system: $a=9.051$ (1), $b=10.229$ (1), $c=18.019$ (2) Å, $\beta=96.00$ (1)°, $Z=2$, space group $P2_1$. The structure has been solved with data collected on an automated diffractometer and refined by full-matrix least squares to $R=0.08$ for 3004 reflexions. The analysis confirms that the acetate group at C(16) is axial (α) and therefore *trans* to the lactone ring.

Introduction

Echinocystic acid (I) is related to the β -amyrin group of triterpenoids, a common feature of which is hydroxylation at the C(16) position (Boar & Allen, 1973). However, the precise stereochemistry at C(16) in echinocystic acid and several other 16-hydroxyoleananes has recently been under dispute (Segal & Taube, 1973). The present paper reports details of the X-ray single-crystal structure analysis of the bromolactone of echinocystic acid diacetate (II). The structure of (II) un-

equivocally establishes the presence of a *trans*-diaxial 16 α ,28-diol system in echinocystic acid (Carlisle, Lindley, Perales, Boar, McGhie & Barton, 1974).



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