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Crystallographic Studies of Dehydrohalogenation in Solid *meso*-Dibromobutane Derivatives.

II.* The Crystal and Molecular Structures of *meso*-β,β'-Dibromoadiponitrile (I), *meso*-(*RSRS*)-α,α'-Dimethyl-β,β'-dibromoadiponitrile (II) and *meso*-(*RRSS*)-α,α'-Dimethyl-β,β'-dibromoadiponitrile (III)

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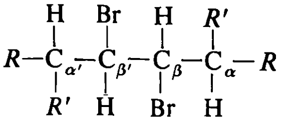
The structures of the title compounds were determined. All crystals are monoclinic with the following space groups and cell dimensions: (I): $C2/c$, a = 13·459 (1), b = 5·372 (1), c = 11·721 (1) Å, β = 100·75 (1)°, Z = 4; (II): $P2_1/n$, a = 5·632 (2), b = 7·175 (1), c = 13·129 (1) Å, β = 96·70 (3)°, Z = 2; (III*a*): $P2_1/n$, a = 6·614 (2), b = 10·186 (3), c = 7·872 (2) Å, β = 91·76 (4)°, Z = 2; (III*b*): $C2/c$, a = 18·101 (5), b = 5·379 (1), c = 11·795 (2) Å, β = 115·36 (2)°, Z = 4. The last isomer [(III*a*), (III*b*)] is dimorphic. The structures were refined to R = 0·056, 0·043, 0·051, and 0·038 respectively. These compounds react with gaseous ammonia or amines to yield the corresponding butadienes by double dehydrobromination. In (II) and (III) the reaction is strictly topochemical; the configurations of the products correlate with the conformations of the starting molecules in the crystal. The lack of topochemical control in β,β'-dibromoadiponitrile probably results from a pre-reaction equilibrium of conformers in the solid. The packing arrangements of these compounds are determined mainly by donor–acceptor and van der Waals interactions.

Introduction

As part of our studies (part I, Rabinovich & Shakked, 1977; Friedman, Gati, Lahav, Rabinovich & Shakked, 1975) on the stereo course of double dehydrohalogenation of solid *meso*-dihalogenobutanes by the reaction of gaseous ammonia or amines, we determined the structures of some *meso*-dibromoadiponitriles [(1): R = CN; R' = H, CH_3].

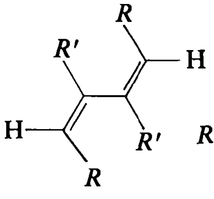


$$R-\overset{\mathrm{H}}{\underset{R'}{\mathrm{C}_{\alpha'}}}-\overset{\mathrm{Br}}{\underset{\mathrm{H}}{\mathrm{C}_{\beta'}}}-\overset{\mathrm{H}}{\underset{\mathrm{Br}}{\mathrm{C}_{\beta}}}-\overset{R'}{\underset{\mathrm{H}}{\mathrm{C}_{\alpha}}}-R$$

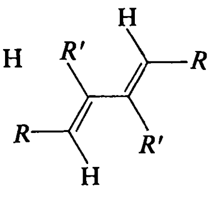
(1)

meso-β,β'-*Dibromoadiponitrile* [(1): R = CN; R' = H]

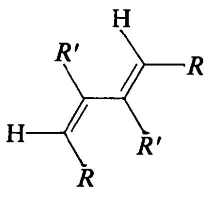
Compound (I) crystallizes in two monoclinic modifications ($C2/c$, Z = 4 and $P2_1/c$, Z = 2). Both forms eliminate to a mixture of the corresponding dinitriles of 1,3-*cis*,*cis*- (2), 1,3-*trans*,*trans*- (3) and 1,3-*cis*,*trans*- (4) butadienes, in the approximate ratio of 2:3:5. The first crystal modification was chosen for our analysis as it yields better specimens for intensity measurements.



(2)



(3)



(4)

meso-α,α'-*Dimethyl*-β,β'-*dibromoadiponitrile* [(1): R = CN; R' = CH_3]

Each of the two possible *meso*-diastereoisomers yields a single product. One of the isomers (II) crystallizes in a single modification and eliminates to the corresponding dinitrile of 1,3-*trans*,*trans*-butadiene (3). The other isomer crystallizes in two modifications [(III*a*) and (III*b*)]. Each modification eliminates to the corresponding 1,3-*cis*,*cis*-butadiene (2); the reaction in (III*a*) is faster than that in (III*b*). We have determined the structures of both forms in order to study the possible effects of the packing arrangement on the reaction rate on one hand, and on the molecular conformation on the other.

Only in (II) and (III) do we observe a direct correlation between the conformations of the starting molecules in the crystal and the configuration of the products. This correlation will be discussed in part III of the present series.

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* Part I: Rabinovich & Shakked (1977).

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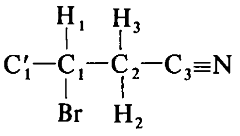
Experimental and structure determination

All the compounds crystallize in monoclinic centrosymmetric space groups, the molecules occupying centres of inversion. Crystal data are in Table 1. Intensities were collected automatically on a Siemens diffractometer (Rabinovich & Shakked, 1977). The agreements between equivalent data sets were: 3%, 1229 reflections (I); 4%, 1160 reflections (II); 5%, 1163 reflections (III*a*); and 3%, 1268 reflections (III*b*). The structures were solved by the heavy-atom technique. Refinement was by full-matrix least-squares as described in part I (Rabinovich & Shakked, 1977). The results of the refinements are given in Table 2. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

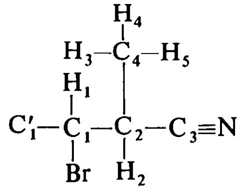
Results

The numbering of the atoms is given below. Atoms related by a centre of symmetry are primed.



$C'_1-C_1(H_1)(Br)-C_2(H_3)(H_2)-C_3\equiv N$

(I)



$C'_1-C_1(H_1)(Br)-C_2(H_2)(C_4H_3H_4H_5)-C_3\equiv N$

(II), (III*a*), (III*b*)

Table 2. *Results of the refinement*

$R = \Sigma|kF_o - |F_c||/\Sigma kF_o$.
$r = \Sigma w(k^2F_o^2 - |F_c|^2)^2/\Sigma wk^4F_o^4$.
$D = [\Sigma w(k^2F_o^2 - |F_c|^2)^2/(n-s)]^{1/2}$.
n = Number of reflections incuded in the last cycle of refinement.
s = Number of refined parameters.

Compound	R	r	D	n	s
(I)	0·056	0·005	1·06	970	58
(II)	0·043	0·003	1·31	941	75
(III*a*)	0·051	0·005	1·28	942	75
(III*b*)	0·038	0·003	1·26	1066	75

Table 3. *Fractional coordinates* ($\times 10^4$, *for* Br $\times 10^5$)

	x	y	z
meso-β,β'-Dibromoadiponitrile (I)			
Br	−8922 (3)	27806 (7)	9269 (4)
C(1)	−530 (3)	−200 (7)	132 (3)
C(2)	−1356 (3)	−681 (8)	−927 (4)
C(3)	−1424 (3)	1283 (4)	−1800 (4)
N	−1465 (3)	2822 (7)	−2468 (4)
meso-(*RSRS*)-*α,α'*-Dimethyl-*β,β'*-dibromoadiponitrile (II)			
Br	25077 (8)	14600 (6)	10446 (3)
C(1)	5247 (7)	113 (5)	575 (3)
C(2)	5562 (8)	−1768 (6)	1156 (3)
C(3)	6216 (8)	−1358 (6)	2262 (3)
C(4)	3444 (13)	−3108 (7)	1000 (4)
N	6705 (7)	−1065 (6)	3115 (3)
meso-(*RRSS*)-*α,α'*-Dimethyl-*β,β'*-dibromoadiponitrile (III*a*)			
Br	2776 (8)	3809 (5)	21253 (5)
C(1)	356 (6)	631 (4)	4609 (5)
C(2)	−871 (6)	1860 (4)	4989 (5)
C(3)	−3023 (8)	1706 (4)	4471 (6)
C(4)	8 (9)	3114 (5)	4270 (9)
N	−4701 (7)	1612 (4)	4052 (6)
meso-(*RRSS*)-*α,α'*-Dimethyl-*β,β'*-dibromoadiponitrile (III*b*)			
Br	7462 (2)	26649 (6)	16393 (3)
C(1)	430 (2)	−233 (5)	513 (3)
C(2)	1084 (2)	−693 (6)	45 (3)
C(3)	1155 (2)	1430 (7)	−691 (3)
C(4)	1922 (2)	−1356 (10)	1104 (4)
N	1207 (3)	3058 (6)	−1261 (4)

Table 1. *Crystal data*

	(I)	(II)	(III*a*)	(III*b*)
Compound	$C_6H_6N_2Br_2$	$C_8H_{10}N_2Br_2$	$C_8H_{10}N_2Br_2$	$C_8H_{10}N_2Br_2$
M_r	265·8	293·8	293·8	293·8
Space group	$C2/c$	$P2_1/n$	$P2_1/n$	$C2/c$
a (Å)	13·459 (1)	5·632 (2)	6·614 (2)	18·101 (5)
b (Å)	5·372 (1)	7·175 (1)	10·186 (3)	5·379 (1)
c (Å)	11·721 (1)	13·129 (1)	7·872 (2)	11·795 (2)
β (°)	100·75 (1)	96·70 (3)	91·76 (4)	115·36 (2)
Z	4	2	2	4
D_c (g cm^{-3})	2·12	1·85	1·84	1·88
D_m (g cm^{-3})	2·10	1·87	1·84	1·90
V (Å^3)	832·6	526·9	530·1	1037·8
μ(Mo $K\alpha$) (cm^{-1})	100·6	81·5	80·6	82·2

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33113 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The atomic parameters are in Tables 3 and 4. Observed bond lengths and angles are in Tables 5 and 6. Short intermolecular distances are in Table 7. Stereoscopic views of the molecules with their thermal ellipsoids scaled to 50% probability (Johnson, 1965) are shown in Figs. 1, 2, 3 and 4. Figs. 5, 6, 7 and 8 show stereoscopic views of the packing arrangements.

Table 4. *Fractional coordinates of* H *atoms* (× 10^3) *and isotropic temperature factors* (× 10^3)

	x	y	z	$\overline{U^2}$ (Å^2)
Compound (I)				
H(1)	−53 (2)	−161 (6)	67 (3)	−11 (9)
H(2)	−119 (4)	−206 (9)	−125 (5)	37 (18)
H(3)	−201 (3)	−76 (7)	−65 (3)	−3 (10)
Compound (II)				
H(1)	685 (6)	101 (5)	78 (2)	2 (9)
H(2)	704 (7)	−236 (6)	94 (3)	21 (12)
H(3)	362 (11)	−427 (8)	139 (3)	64 (18)
H(4)	284 (10)	−340 (7)	21 (4)	64 (18)
H(5)	206 (9)	−272 (8)	117 (4)	46 (21)
Compound (III*a*)				
H(1)	180 (6)	80 (3)	480 (5)	3 (10)
H(2)	−87 (7)	194 (4)	614 (6)	28 (13)
H(3)	1 (7)	312 (6)	283 (7)	58 (18)
H(4)	142 (10)	312 (6)	446 (8)	75 (23)
H(5)	−66 (8)	382 (5)	452 (6)	35 (15)
Compound (III*b*)				
H(1)	41 (2)	−155 (6)	101 (3)	−4 (7)
H(2)	91 (2)	−199 (5)	−46 (3)	−7 (7)
H(3)	189 (4)	−246 (8)	176 (5)	64 (17)
H(4)	218 (3)	4 (9)	164 (5)	53 (17)
H(5)	229 (3)	−185 (8)	82 (4)	29 (13)

Table 5. *Bond lengths* (Å), *angles* (°) *and e.s.d.'s of meso-β,β'-dibromoadiponitrile* (I)

C(1)–C(1′)	1·530 (8)	C(1′)–C(1)–C(2)	115·1 (4)
C(1)–Br	1·962 (4)	C(1′)–C(1)–Br	108·0 (3)
C(1)–C(2)	1·527 (5)	C(2)–C(1)–Br	108·3 (3)
C(2)–C(3)	1·461 (6)	C(1)–C(2)–C(3)	112·8 (4)
C(3)–N	1·133 (6)	C(2)–C(3)–N	179·1 (4)
C(1)–H(1)	0·99 (3)	H(1)–C(1)–C(1′)	111 (2)
C(2)–H(2)	1·00 (4)	H(1)–C(1)–Br	107 (2)
C(2)–H(3)	0·88 (6)	H(1)–C(1)–C(2)	108 (2)
		H(2)–C(2)–C(1)	107 (4)
		H(2)–C(2)–C(3)	107 (4)
		H(2)–C(2)–H(3)	114 (5)
		H(3)–C(2)–C(1)	107 (2)
		H(3)–C(2)–C(3)	109 (2)

Table 6. *Bond lengths* (Å), *angles* (°) *and e.s.d.'s of meso-*(*RSRS*)*-α,α'-dimethyl-β,β'-dibromoadiponitrile* (II) *and meso-*(*RRSS*)*-α,α'-dimethyl-β,β'-dibromoadiponitrile* (III*a,b*)

	(II)	(III*a*)	(III*b*)
C(1)–C(1′)	1·513 (7)	1·507 (7)	1·528 (6)
C(1)–Br	1·979 (4)	1·971 (4)	1·967 (3)
C(1)–C(2)	1·550 (5)	1·526 (6)	1·525 (6)
C(2)–C(3)	1·486 (6)	1·476 (7)	1·474 (5)
C(3)–N	1·141 (5)	1·152 (7)	1·133 (6)
C(2)–C(4)	1·527 (8)	1·521 (7)	1·539 (6)
C(1)–H(1)	1·12 (3)	0·98 (4)	0·93 (3)
C(2)–H(2)	1·00 (4)	0·91 (5)	0·88 (3)
C(4)–H(3)	0·98 (6)	1·13 (6)	1·00 (8)
C(4)–H(4)	1·08 (5)	0·94 (7)	0·97 (5)
C(4)–H(5)	0·88 (5)	0·87 (6)	0·89 (7)
C(1′)–C(1)–C(2)	113·3 (3)	116·4 (3)	115·1 (3)
C(1′)–C(1)–Br	107·7 (3)	107·2 (2)	107·9 (2)
C(2)–C(1)–Br	108·7 (3)	107·6 (3)	109·0 (2)
C(1)–C(2)–C(3)	108·0 (3)	111·9 (3)	111·4 (3)
C(1)–C(2)–C(4)	116·1 (4)	113·8 (4)	113·1 (2)
C(3)–C(2)–C(4)	110·9 (4)	111·3 (4)	110·7 (3)
C(2)–C(3)–N	179·1 (5)	178·5 (5)	179·7 (4)
H(1)–C(1)–C(1′)	111 (2)	114 (2)	109 (2)
H(1)–C(1)–Br	106 (2)	100 (2)	105 (2)
H(1)–C(1)–C(2)	110 (2)	110 (2)	111 (2)
H(2)–C(2)–C(1)	106 (2)	106 (2)	106 (2)
H(2)–C(2)–C(3)	104 (2)	105 (3)	107 (2)
H(2)–C(2)–C(4)	111 (2)	108 (3)	108 (2)
H(3)–C(4)–C(2)	116 (3)	113 (3)	113 (3)
H(4)–C(4)–C(2)	114 (3)	110 (4)	112 (3)
H(5)–C(4)–C(2)	118 (4)	114 (3)	113 (5)
H(3)–C(4)–H(4)	97 (4)	97 (5)	97 (6)
H(3)–C(4)–H(5)	100 (5)	104 (5)	105 (5)
H(4)–C(4)–H(5)	110 (4)	118 (5)	114 (5)

The analyses established the configuration of (II) as (*RSRS*) and that of (III*a*) and (III*b*) as (*RRSS*).

Discussion

The molecular conformation and the course of the double-elimination reaction will be discussed in part III. Here we discuss the geometry of the dibromobutane moiety of the present adiponitriles and the two dimethyl

Table 7. *Short intermolecular distances* (Å) *in the nitriles*

The second atom in each pair is related to the first by the corresponding symmetry and translation operations.

	(I)	(II)	(III*a*)	(III*b*)
Br···Br	4·02 $[\bar{x}, y, \frac{1}{2}-z; 000]$		3·44 $[\bar{x},\bar{y},\bar{z}; 000]$	4·02 $[\bar{x}, y, \frac{1}{2}-z; 000]$
Br···N	3·20 $[x, \bar{y}, \frac{1}{2}+z; 010]$	3·26 $[\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z; 000]$		3·22 $[x, \bar{y}, \frac{1}{2}+z; 010]$
N···C(2)	3·27 $[\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z; \bar{1}0\bar{1}]$			

adipates (part I, Rabinovich & Shakked, 1977) [referred to as (IV) and (V)], the geometry of the nitrile group and the packing of the adiponitriles.

Bond lengths and angles

The bond lengths and angles of the dibromobutane moiety of the six molecules are given in Table 8.

The bond scatter in all cases is larger than the average e.s.d. and in some cases the individual bond lengths differ from the average by as much as 3σ. However, in view of the fact that the least-squares method tends to underestimate the e.s.d. in positional parameters, these deviations may be considered as insignificant and the average values obtained for chemically equivalent bonds may be taken as representative values.

Similar C—C lengths were observed in adipic acid (Housty & Hospital, 1965) and dimethyl *meso*-β,β'-dichloroadipate (Kaufman, Rabinovich & Schmidt, 1974). The observed bond angles at C(1) are similar for the six molecules. The large values of the C(1')—C(1)—C(2) angles compared with an ideal sp^3 hybridization result from the steric repulsions caused by the bulky substituents attached to C(2), and the relatively large angle scatter (1·6°) is significant.

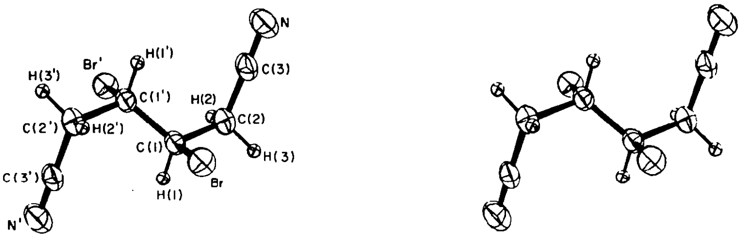


Fig. 1. Stereoscopic view of *meso*-β,β'-dibromoadiponitrile (I).

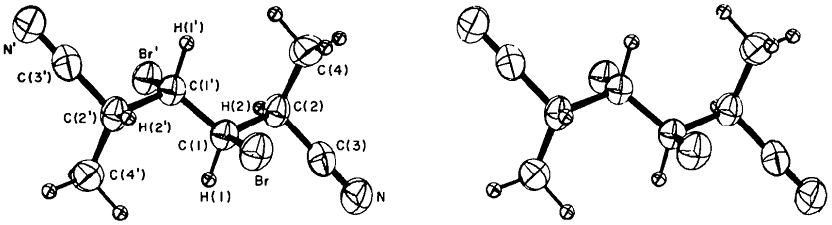


Fig. 2. Stereoscopic view of *meso*-(*RSRS*)-α,α'-dimethyl-β,β'-dibromoadiponitrile (II).

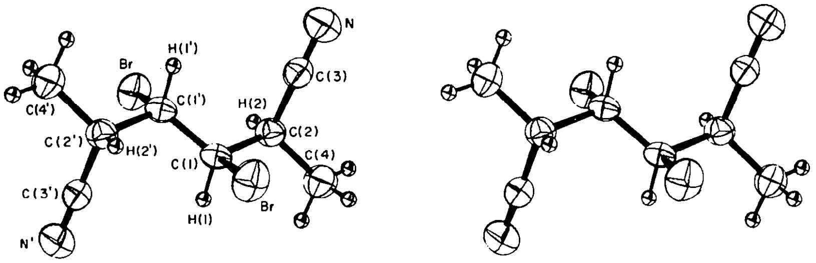


Fig. 3. Stereoscopic view of *meso*-(*RRSS*)-α,α'-dimethyl-β,β'-dibromoadiponitrile (III*a*).

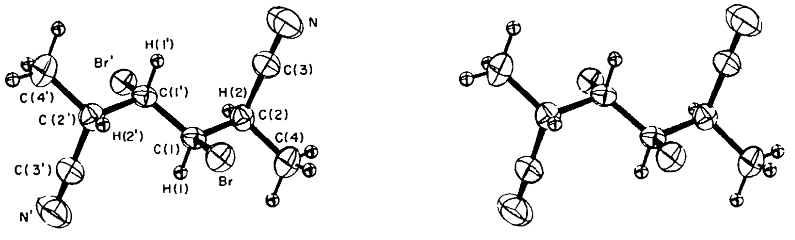


Fig. 4. Stereoscopic view of *meso*-(*RRSS*)-α,α'-dimethyl-β,β'-dibromoadiponitrile (III*b*).

The geometry of the C—C≡N *group*

Examination of various structures incorporating nitrile groups shows that the hybridization state of the first C atom and the number of nitrile groups attached to it affect the length of the C—C_{sp} single bond. Its length varies for example from 1·49 Å in the present structures (Table 6) to 1·40 Å in sodium tricyanomethanide (Andersen, Klewe & Thom, 1967). To compare the dimensions of the C—C≡N group in the adiponitriles with those of similar molecules, we have chosen several recently determined structures where a single nitrile group is attached to a C_{sp^3} atom. The results are given in Table 9. The scatter of the C—C bond is slightly larger than that of the C≡N bond, indicating the influence of different adjacent bonds, but still the fluctuations in the two bond types seem to result mainly from random errors. The average value of

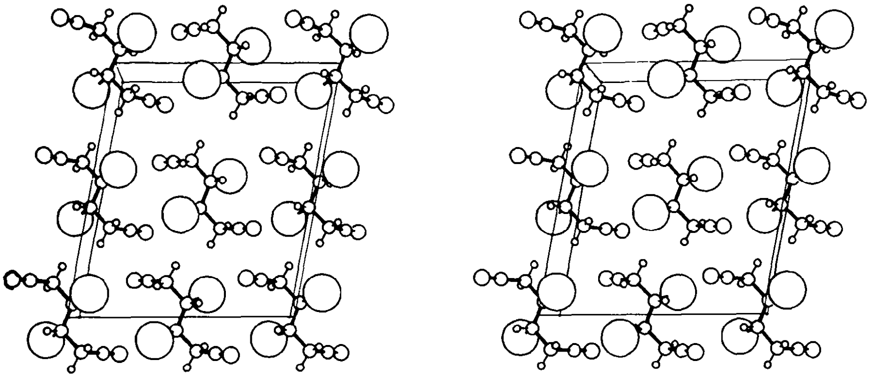


Fig. 5. Stereoscopic view of the packing arrangement of (I) viewed down **b**.

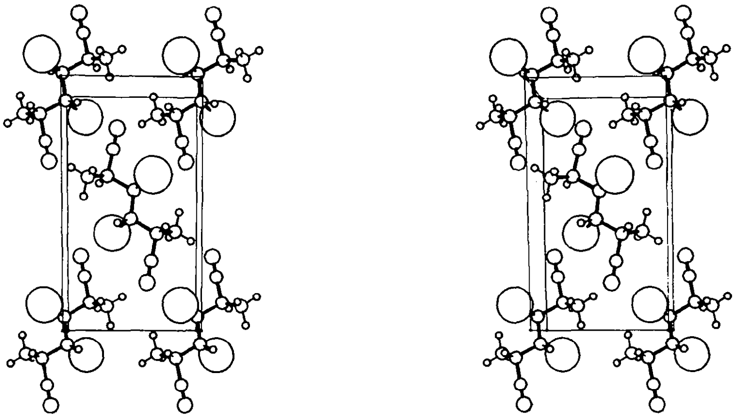


Fig. 6. Stereoscopic view of the packing arrangement of (II) viewed down **a**.

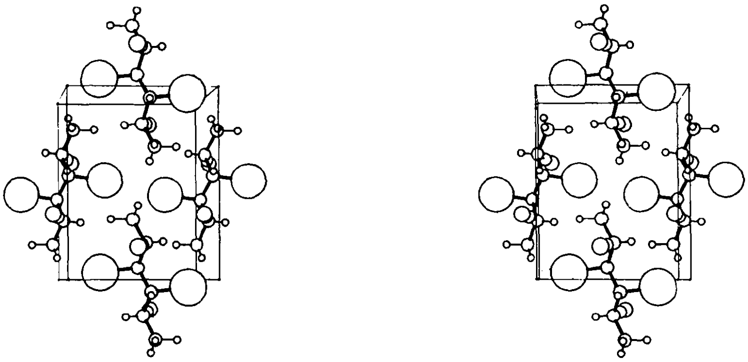


Fig. 7. Stereoscopic view of the packing arrangement of (III*a*) viewed down **a**.

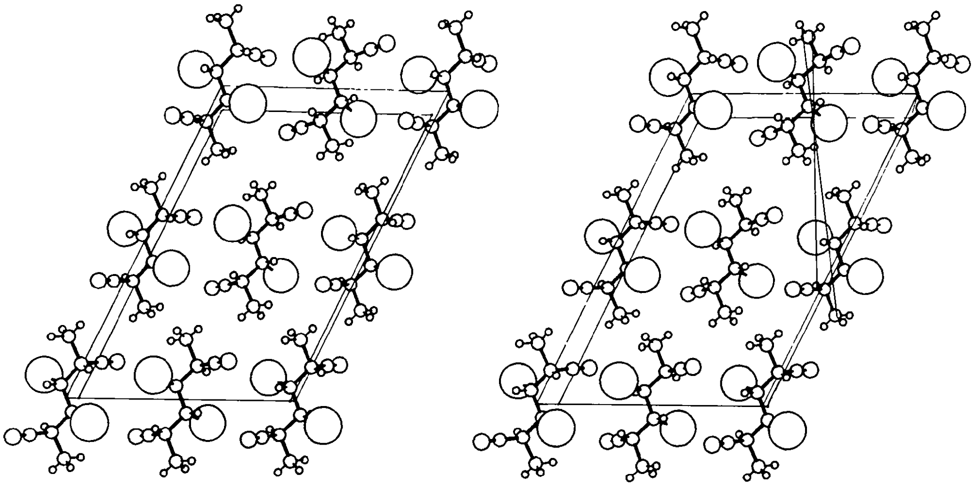


Fig. 8. Stereoscopic view of the packing arrangement of (III*b*) viewed down **b**.

Table 8. *Bond lengths* (Å) *and angles* (°) *of the dibromobutane moiety*

	(I)	(II)	(III*a*)	(III*b*)	(IV)	(V)	Average	Average e.s.d.	Bond scatter
C(1)–C(1′)	1·530	1·513	1·507	1·528	1·517	1·508	1·517	0·007	0·010
C(1)–Br	1·962	1·979	1·971	1·967	1·981	1·982	1·974	0·004	0·008
C(1)–C(2)	1·527	1·550	1·526	1·525	1·530	1·548	1·534	0·006	0·011
C(2)–CH_3		1·527	1·521	1·539	1·510	1·528	1·525	0·007	0·011
C(1′)–C(1)–C(2)	115·1	113·3	116·4	115·1	116·1	118·1	115·7	0·3	1·6
C(1′)–C(1)–Br	108·0	107·7	107·2	107·9	107·4	107·4	107·6	0·3	0·3
C(2)–C(1)–Br	108·3	108·7	107·6	109·0	107·8	107·6	108·2	0·3	0·6

Table 9. *Bond lengths* (Å) *and angles* (°) *of the* C–C≡N *group in aliphatic nitriles*

Compound	C–C	C≡N	C–C≡N
1(I)	1·461	1·133	179·1
2(II)	1·486	1·141	179·1
3(III*a*)	1·476	1·152	178·5
4(III*b*)	1·474	1·133	179·7
5	1·453	1·121	177·9
6	1·456	1·134	179·0
7*a*	1·471	1·134	176·3
7*b*	1·478	1·135	177·0
8	1·479	1·151	178·0
9	1·478	1·142	178·8
10	1·467	1·127	178·9
11*a*	1·454	1·151	176·8
11*b*	1·450	1·149	178·4
Average ($\bar{r}$)	1·486	1·139	178·3
Bond scatter (*s*)*	0·012	0·010	1·0

References: (1), (2), (3), (4) This work. (5) Chieh (1973). (6) Klewe (1971). (7) Jaffe, Malament, Slisz & McBride (1972). (8) Malmstrom & Cordes (1973). (9) Aasen, Iversen & Klewe (1975). (10) Roques, Guy & Fourme (1976). (11) Harel & Hirshfeld (1975).

* $s = [\Sigma(r_i - \bar{r})^2/(n-1)]^{1/2}$.

the C≡N bond (1·14 Å) is significantly below the accepted spectroscopic value (Britton, 1967) of 1·158 Å. This bond shortening arises largely from the neglect of internal vibrations (Harel & Hirshfeld, 1975). The average departure from linearity at the C–C≡N angle seems to be insignificant although some of the individual departures are significant and probably result from steric effects.

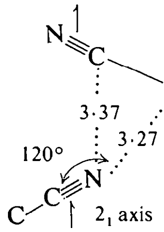
Molecular packing

The packing arrangements of the adiponitriles are determined mainly by donor–acceptor and van der Waals interactions.

The former involves Br···N≡C and C···N≡C interactions. The observed Br···N contacts in (I), (II) and (III*b*) (3·20, 3·26 and 3·22 Å respectively, Table 7) are significantly shorter than the quoted van der Waals distance of 3·45 Å (Pauling, 1960) and may be regarded as weak Lewis acid–base interactions (Britton, 1967). These interactions in (I) and (III*b*) are associated with a nearly linear arrangement, the Br···N≡C angles being 164 and 162° respectively.

The corresponding angle in (II) is 97°. Similar Br···N contacts are observed in bromotricyanomethane (Witt, Britton & Mahon, 1972) and in 2,4,6-tribromobenzonitrile (Carter & Britton, 1972). Shorter contacts (<3·0 Å) are observed in halogen cyanides and are attributed by Britton (1967) to the fact that the halogens in these compounds are attached to more electronegative groups which increase their acceptor or Lewis acid strengths.

Interactions of the type C···N≡C are observed only in (I). If we accept 3·4 Å as the van der Waals distance for C···N with no acid–base character (Witt, Britton & Mahon, 1972), then the observed C···N contact of 3·27 Å in (I) indicates a weak acid–base interaction. This contact exists between the N atom and C_α whereas the contact between the N and the nitrile C atom is longer (3·37 Å):



Similar interactions are observed in tetracyanocyclobutane (Greenberg & Post, 1968) and tetracyanomethane (Britton, 1974). However, the acid site in tetracyanomethane is not localized on the central atom but also involves three adjacent cyanide C atoms with shorter C···N contacts varying from 3·0 to 3·19 Å. The C···N distances to the central atom (3·20, 3·26 Å) are similar to that observed in (I). The absence of such interactions in (II), (III*a*) and (III*b*) may be attributed to the partial screening of the C_α atom by the methyl group. This argument is further supported by comparing the packing arrangements of (I) and (III*b*). The packing modes of the two compounds are very similar in the *bc* plane, as is reflected by the cell dimensions (Table 1) and by the N···Br and Br···Br contacts (Table 7, Figs. 5 and 8). However, the substitution of one of the H_α atoms in (I) by a methyl group as in (III*b*) prevents close N···C≡N contacts, thus leading to a different packing arrangement along **a**.

The observed Br···Br contacts in (I) and (III*b*) are similar to the quoted van der Waals distance (3·9 Å). However, the molecular packing of (III*a*) (Fig. 7) which is determined mainly by short Br···Br contacts across centres of inversion involves a distance of 3·44 Å which is considerably shorter than the usually reported Br···Br contacts in substituted organic molecules of intermediate complexity. The intermolecular angle of the centrosymmetric system, C–Br···Br–C, is 173°. This contact is similar to that observed in 2,4-dibromomenthone (3·52 Å) (Wunderlich & Lipscomb, 1960) and in Br_2 crystals (3·30 Å) (Wyckoff, 1963). An exceptionally short contact (3·32 Å) in triphenylmethyl bromide (Stora, 1953) was attributed to partial ionization of the C–Br bond. The nearly linear arrangement of C–Br···Br–C in (III*a*) is in accordance with findings (Sakurai, Sundaralingam & Jeffrey, 1963) on Cl···Cl interactions, namely, that very short contacts are associated with a nearly linear arrangement, thus suggesting that the van der Waals contact is not necessarily isotropic. Bent (1968) suggests that the nearly linear short halogen···halogen interaction results from the merging of the electron clouds of two halogen atoms whose spin sets are anticoincident.

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