

## Structural Chemistry of the 8,8-Dicyanoheptafulvene System.

### II.\* The Crystal and Molecular Structure of 1,6-Dimethyl-8,8-dicyanoheptafulvene

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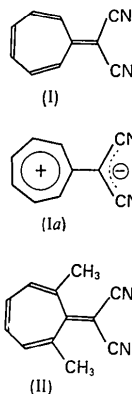
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1,6-Dimethyl-8,8-dicyanoheptafulvene,  $C_{12}H_{10}N_2$ , crystallizes in yellow plates, space group  $P2_1/c$ , with  $a=8.787$  (3),  $b=13.274$  (3),  $c=9.157$  (3) Å,  $\beta=104.21$  (3)° and  $Z=4$ . The crystal structure was solved by the symbolic addition method and refined by the full-matrix least-squares method. The final  $R$  value was 0.086. The molecule has essentially  $m$  symmetry through the exocyclic double bond. The seven-membered ring takes a deep boat form and has a definite bond alternation. Some structural-chemical features of the 8,8-dicyanoheptafulvene system are discussed.

#### Introduction

The molecule of 8,8-dicyanoheptafulvene (I), a stable derivative of a non-alternant hydrocarbon, is completely planar, and a considerable contribution from the dipolar ionic form (Ia) to the ground-state structure should be taken into account (Shimanouchi, Ashida, Sasada, Kakudo, Murata & Kitahara, 1966).



In connexion with the current controversy over the aromaticity of the non-benzenoid aromatic seven-membered ring compounds (Bertelli, Andrews & Crews, 1969), it is of structural-chemical interest to examine the molecular deformability of this system. Of several substituted compounds so far synthesized (Oda, 1967), 1,6-dimethyl-8,8-dicyanoheptafulvene (II) was chosen for the present study. A preliminary report has already been published (Shimanouchi, Sasada, Kabuto & Kitahara, 1968).

#### Experimental

1,6-Dimethyl-8,8-dicyanoheptafulvene (1,6-dimethyl-8,8-dicyanomethylenecycloheptatriene) crystallizes

from benzene-cyclohexane solution in the form of yellow plates. The crystal data are:  $C_{12}H_{10}N_2$ , M.W. 182.2, m.p. 102–103°C. Monoclinic,  $a=8.787 \pm 0.003$ ,  $b=13.274 \pm 0.003$ ,  $c=9.157 \pm 0.003$  Å,  $\beta=104.21 \pm 0.03^\circ$ ,  $U=1035.4$  Å<sup>3</sup>,  $D_m=1.15$  g cm<sup>-3</sup> (by flotation),  $D_x=1.17$  g cm<sup>-3</sup>,  $Z=4$ ,  $F(000)=384$ ,  $\mu=0.754$  cm<sup>-1</sup> (Mo  $K\alpha$ ). Systematic absences:  $h0l$  when  $l$  is odd and  $0k0$  when  $k$  is odd. Space group  $P2_1/c$ .

A crystal of dimensions 0.20 × 0.20 × 0.25 mm was mounted about the  $c$  axis (0.25 mm) and placed on a Rigaku automatic four-circle diffractometer. The unit-cell dimensions were determined by a least-squares refinement with the angles for 12 reflexions centred manually on the diffractometer. The intensity data were obtained using Mo  $K\alpha$  radiation, the  $\theta$ - $2\theta$  scan technique being applied with a  $2\theta$  speed of 2° min<sup>-1</sup>. The backgrounds at both limits of the scan range given by  $2.0^\circ + 1.0^\circ \tan \theta$  were measured for 10 s. Attenuators were inserted when the counting rate exceeded 8000 counts s<sup>-1</sup>. A pulse-height analyser and a zirconium filter were used. 1235 reflexions out of 2470 in the  $2\theta$  range 0–55° were considered to have intensities significantly above zero, the threshold value being  $3\sigma(F_o)$ . All intensities were corrected for decay according to the intensity decrease of the three monitoring reflexions measured at every 62 reflexions. Lorentz and polarization factors were taken into account as usual, but no absorption and extinction corrections were made. The appearance of the crystal did not change during the period of data collection.

#### Structure determination

By the manual symbolic addition method (Karle & Karle, 1966), the signs for 230 reflexions were determined out of 340 with  $|E| \geq 1.5$ . The  $E$  map synthesized with these reflexions revealed all the non-hydrogen atoms. Block-diagonal matrix least-squares refinement using unit weights gave an  $R$  value of 0.120. The sub-

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Table 1. *Final atomic parameters with their e.s.d.'s*

(a) Heavy atoms.

The anisotropic temperature factors are expressed in the form:  $\exp \{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\}$ .Positional parameters are  $\times 10^4$ , thermal parameters  $\times 10^5$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
C(1)	4096 (6)	407 (4)	-2738 (5)	1642 (86)	550 (32)	988 (61)	332 (88)	444 (119)	84 (71)
C(2)	5562 (6)	735 (4)	-2139 (6)	1261 (77)	863 (42)	1349 (75)	589 (101)	630 (125)	106 (92)
C(3)	6072 (6)	1563 (4)	-1160 (6)	1182 (81)	769 (41)	1735 (89)	-122 (95)	136 (137)	95 (103)
C(4)	5289 (6)	1951 (4)	-209 (6)	1577 (88)	596 (35)	1432 (79)	-444 (95)	-208 (140)	-188 (87)
C(5)	3815 (6)	1643 (4)	-19 (5)	1615 (88)	678 (35)	976 (63)	296 (94)	350 (119)	7 (83)
C(6)	2662 (5)	1174 (4)	-1006 (5)	1149 (71)	714 (35)	1052 (64)	190 (81)	379 (109)	349 (77)
C(7)	2711 (5)	970 (3)	-2561 (5)	1295 (73)	480 (29)	971 (59)	-284 (75)	376 (103)	57 (67)
C(8)	1509 (5)	1212 (4)	-3759 (5)	1106 (70)	703 (35)	1083 (67)	-44 (82)	155 (107)	106 (76)
C(9)	1588 (7)	1027 (4)	-5265 (6)	1884 (98)	834 (43)	1205 (77)	453 (106)	-308 (134)	120 (92)
C(10)	154 (7)	1735 (5)	-3613 (6)	1349 (87)	1052 (51)	1431 (80)	171 (111)	-155 (133)	14 (103)
C(11)	3808 (11)	-574 (5)	-3589 (8)	2892 (161)	772 (50)	1576 (104)	757 (154)	-118 (219)	-696 (115)
C(12)	1214 (8)	790 (9)	-529 (8)	1621 (110)	1985 (105)	1336 (96)	-676 (181)	1186 (166)	203 (170)
N(1)	1649 (7)	909 (5)	-6483 (6)	3469 (145)	1527 (61)	1187 (77)	1235 (154)	-153 (162)	-80 (108)
N(2)	-956 (7)	2145 (5)	-3536 (7)	1645 (94)	1701 (68)	2613 (117)	1248 (131)	221 (163)	311 (134)

Table 1 (*cont.*)

(b) Hydrogen atoms.

Positional parameters are  $\times 10^3$ 

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
H(2)	647 (7)	36 (4)	-251 (6)	3.9 (1.3)
H(3)	723 (7)	185 (4)	-108 (6)	3.9 (1.3)
H(4)	580 (6)	249 (4)	51 (6)	2.5 (1.1)
H(5)	356 (6)	183 (4)	104 (6)	3.7 (1.3)
H(11)	481 (10)	-90 (6)	-352 (8)	7.2 (2.2)
H(12)	339 (9)	-46 (5)	-466 (9)	6.8 (2.0)
H(13)	303 (10)	-95 (6)	-314 (8)	7.3 (2.5)
H(14)	32 (9)	125 (5)	-97 (8)	6.0 (2.0)
H(15)	137 (7)	94 (4)	55 (7)	4.2 (1.4)
H(16)	100 (12)	8 (8)	-92 (11)	12.2 (4.0)

sequent difference map clearly located all the hydrogen atoms with peak heights greater than  $0.3 \text{ e \AA}^{-3}$ . From this fact it is concluded that the methyl groups do not rotate in the crystal. The structural parameters of the atoms including isotropic hydrogen were refined by the full-matrix least-squares method minimizing the quantity  $\sum w(|F_o| - |F_c|)^2$ . Weights  $w$  were:  $w = (\sigma^2 + 0.06869|F_o| - 0.00048|F_o|^2)^{-1}$  for the observed reflexions where  $\sigma^2$  is the variance of  $|F_o|^2$  estimated from the counting statistics and  $w=0$  for the unobserved ones. The final  $R$  value was 0.086 for the observed reflexions. An analysis of the weighting scheme (Cruickshank, 1965) at the end of this refinement gave a satisfactory result.

The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1968). The final atomic coordinates and the temperature factors are given in Table 1.\*

\* The structure-factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30333 (10 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The computations were carried out on a HITAC 5020E computer in the University of Tokyo and on a HITAC 8700 computer in Tokyo Institute of Technology. The programs in the Universal Crystallographic Computation Program System (1967) were

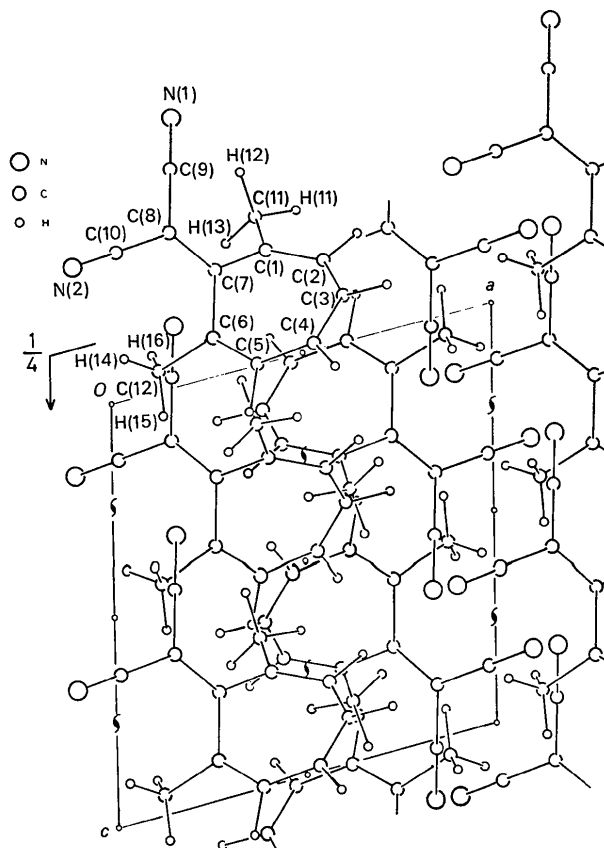
Fig. 1. The crystal structure viewed along the *b* axis.

Table 2. Short intermolecular distances

Atom in position A	Atom in position B	Distance
Between heavy atoms shorter than 3.5 Å		
C(12)	C(12)	3.302 Å
Between heavy and hydrogen atoms shorter than 3.0 Å		
C(12)	H(16)	2.86
Between hydrogen atoms shorter than 2.6 Å		
H(15)	H(16)	2.58
Position A	General coordinates	
B	$x, y, z$	
	$\bar{x}, \bar{y}, \bar{z}$	

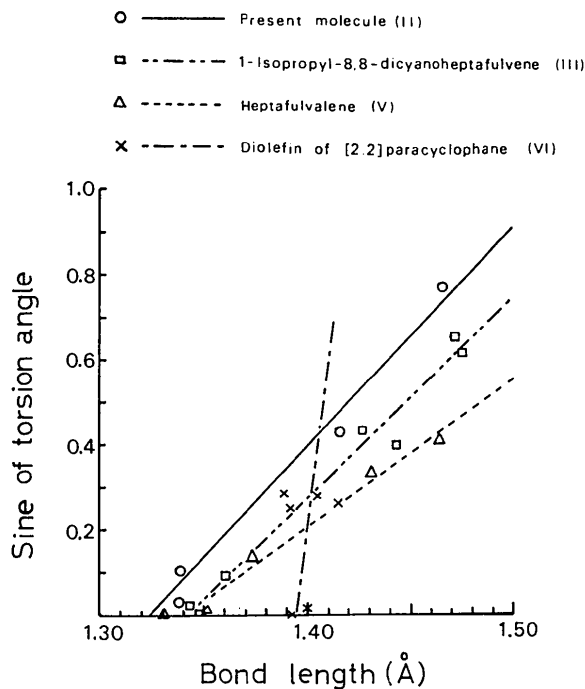
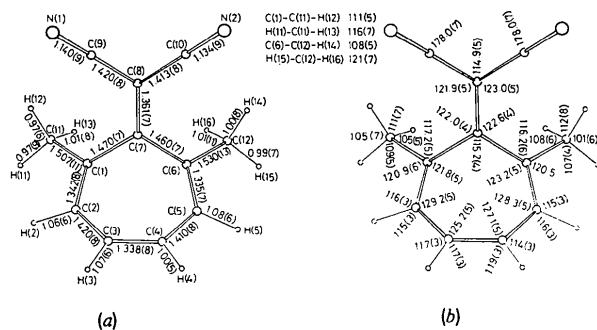


Fig. 2. Relation between the sine of the torsion angle and the C-C bond length.

Fig. 3. Bond distances (Å) and angles ( $^{\circ}$ ). The corresponding e.s.d.'s, given in parentheses, refer to the last decimal positions.

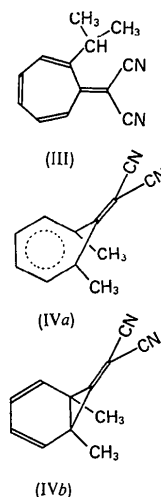
used with some modifications. The programs *XFMLS* for full-matrix least-squares refinement (Ashida, 1971) and *DEAM* for plotting of the thermal ellipsoid (Takanaka, 1972) were also used.

## Results and discussion

A view of the crystal structure is given in Fig. 1, and as shown in Table 2 there are no abnormally short contacts which may seriously affect the molecular conformation.

The most striking result of this study is the major conformational change in the seven-membered ring arising from the introduction of the two methyl groups. As shown in Table 3, the seven-membered ring in the present molecule adopts a deep boat form, while that in (I) is completely planar (Shimanouchi, Ashida, Sasada, Kakudo, Murata & Kitahara, 1966). A seven-membered ring with planar geometry would have impossibly short intramolecular contacts between the cyano carbon and the methyl hydrogen atoms. By taking a boat form, the ring can minimize crowding.

In order to compare the boat forms of the related compounds, the angles  $\delta_1$ ,  $\delta_2$  and  $\delta_3$ , are listed in Table 4. While  $\delta_1$  in the present molecule is remarkably greater than that in 1-isopropyl-8,8-dicyanoheptafulvene (III) (Shimanouchi, Sasada, Kabuto & Kitahara, 1974), there is no difference in  $\delta_2$  between the two compounds.



In connexion with this fact, the norcaradiene character (IVa, IVb) was suspected, because the  $C(1) \cdots C(6)$  interaction might increase  $\delta_1$  and decrease  $\delta_2$  (Ammon, Watts & Stewart, 1970). The overlap integral  $S$  of the  $2p$  orbitals of C(1) and C(6) was calculated using the tables of Mulliken, Rieke, Orloff & Orloff (1949). The  $2p$  orbitals were assumed to be normal to their respective planes (planes 11 and 12 in Table 3). The calculated value of 0.051 for  $S_{16}$  is smaller than that of 0.072 for the cycloheptatriene ring of *tujiic acid* and slightly larger than that for  $S_{13}$  in *trans*-1,3-butadiene (Davis

& Tulinsky, 1966). From these estimations, it is concluded that there is no definite evidence for norcaradiene character in the present molecule.

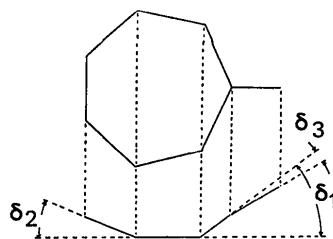
The largest torsion angles  $\theta$  are observed in the C(1)–C(7) and C(6)–C(7) bonds (Table 5). When there is an appreciable amount of torsion in the bond, the overlap between the carbon  $\pi$  orbitals is decreased. The over-

lap integral is proportional to  $\cos \theta$ , and the restoring force against deformation will be approximately proportional to its negative derivative,  $\sin \theta$  (Thomas & Coppens, 1972). A plot of  $\sin \theta$  (for which  $\theta$  was averaged for chemically equivalent bonds) against the bond length is shown in Fig. 2 together with the plots for heptafulvalene (V) (Thomas & Coppens, 1972) and

Table 3. *Some least-squares planes*

The equations of the planes are expressed in the form  $lx' + my' + nz' + p = 0$ , where  $x' = x + z \cos \beta$ ,  $y' = y$  and  $z' = z \sin \beta$ .

Distances marked with an asterisk refer to atoms defining the plane.												
Plane	1	2	3	4	5	6	7	8	9	10	11	12
<i>l</i>	0.0339	-0.5082	0.2917	-0.2036	0.3325	-0.4834	-0.4671	-0.1955	0.3988	-0.4902	-0.1961	0.3807
<i>m</i>	-0.8211	-0.8609	-0.6350	-0.5586	-0.8970	-0.8734	-0.8830	-0.4921	-0.8745	-0.8716	-0.5068	-0.8807
<i>n</i>	0.5697	0.0250	0.7154	0.8040	0.2914	0.0598	0.0455	0.8483	0.2761	-0.0017	0.8395	0.2818
<i>p</i>	1.694	2.668	0.415	3.138	0.825	2.655	2.621	3.140	0.574	2.459	3.140	0.648
Deviations of atoms (Å)												
C(1)	0.008*	0.000*	-0.437	0.024*	1.033	0.000*		-0.012		-0.075	0.000*	1.092
C(2)	-0.007*	-0.947	0.003*	-0.026*				0.000*			0.000*	
C(3)	-0.407		-0.007*	0.012*	0.524	-1.924	-1.872				0.127	
C(4)	-0.379		0.007*	0.587	0.009*	-1.887	-1.867					0.102
C(5)	0.007*	-0.916	-0.003*		-0.020*				0.000*			0.000*
C(6)	-0.008*	0.000*	-0.466	1.027	0.020*	0.000*			-0.013	-0.156	1.098	0.000*
C(7)	-0.558	0.000*	-1.166	-0.010*	-0.008*	-0.035	0.000*	0.000*	0.000*	-0.109	0.000*	0.000*
C(8)	-1.455	0.096		-0.886	-0.869	0.000*	0.034	-0.907	-0.889	-0.003*	-0.902	-0.883
C(9)	-2.002	0.067					0.000*			0.014*		
C(10)	-1.992	0.124					0.000*			-0.007*		
C(11)	0.645	1.134		0.157				0.000*			0.038	
C(12)	0.605	1.151			0.142				0.000*			0.044
N(1)	-2.477	0.009								-0.008*		
N(2)	-2.435	0.161								0.004*		
Interplanar angles (°)												
Plane	2	3	4	5	6	7	8	9	10	11	12	
1	45.3	20.1	24.5	24.0	42.7	42.7	28.3	27.3	45.7	27.4	26.3	
2		65.4	52.8	52.4	2.6	2.9	57.0	56.1	1.9	56.2	55.1	
3			29.5	29.0	62.8	62.8	30.4	29.6	65.8	30.1	29.3	
4				48.1	50.6	51.3	4.6	51.0	54.2	3.6	50.1	
5					50.2	49.5	51.4	4.1	51.8	50.7	3.0	
6						1.4	54.9	54.0	3.5	54.0	53.0	
7							55.6	53.2	3.1	54.7	52.2	
8								54.1	58.4	1.0	53.3	
9									55.5	53.4	1.1	
10										57.6	54.5	
11											52.5	

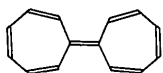
Table 4. *Comparison of planarity of seven-membered rings*

Compound	$\delta_1$	$\delta_2$	$\delta_3$	Reference
Heptafulvalene (V)	24.7	15.7	6.7	Thomas & Coppens (1972).
1-Isopropyl-8,8-dicyanoheptafulvene (III)	37.3	19.5	5.6	Shimanouchi <i>et al.</i> (1974).
1,6-Dimethyl-8,8-dicyanoheptafulvene (II)	45.3	20.1	4.0	Present work.

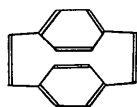
Table 5. *Torsion angles in the seven-membered ring*

C(7) [C(1) C(2)] C(3)	-6.7°
C(1) [C(2) C(3)] C(4)	-26.4
C(2) [C(3) C(4)] C(5)	2.0
C(6) [C(5) C(4)] C(3)	24.7
C(7) [C(6) C(5)] C(4)	5.4
C(1) [C(7) C(6)] C(5)	-55.1
C(6) [C(7) C(1)] C(2)	56.2
C(8) [C(7) C(1)] C(2)	-128.6
C(8) [C(7) C(6)] C(5)	129.7

1-isopropyl-8,8-dicyanoheptafulvene (III) (Shimanouchi, Sasada, Kabuto & Kitahara, 1974).



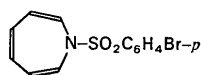
(V)



(VI)

The larger slope for (II) and (III) than for (V) indicates that the seven-membered ring is more rigid in (I) than in (V). In fact, in truly aromatic systems, for example the diolefin of [2.2]paracyclophane (VI) (Coulter & Trueblood, 1963), the forced deformation has little effect on the bond lengths of the benzene ring as shown in Fig. 2. This suggests that in spite of the bond-angle strain in the seven-membered ring the 8,8-dicyanoheptafulvene system has a greater tendency to preserve planarity than (V).

One possible interpretation may be that the bond-angle strain is merely overcome by the  $\pi$ -stabilization energy of the polyene. However, if this were true, the 1*H*-azepine derivative (VII) (Paul, Johnson, Paquette, Barrett & Haluska, 1968), in which the nitrogen atom has trigonal symmetry, should take a planar form, not a deep boat as it does.

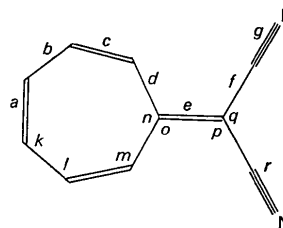


(VII)

It may therefore be indicated that the  $\pi$ -electron delocalization inferred in (I) results from the contribution from the  $6\pi$  dipolar structure which is induced by the strong electron-attracting dicyanomethylene group. That is, the aromatic sextet appears to play an important role in stabilizing the 8,8-dicyanoheptafulvene structure. This consideration leads to the supposition that the seven-membered ring in heptafulvalene (V), of which the non-planarity has been discussed recently (Cheng & Nyburg, 1973; Coppens, 1973), has less tendency to preserve planarity than in (I).

Table 6. *Comparison of bond lengths and angles between 8,8-dicyanoheptafulvene (I) and 1,6-dimethyl-8,8-dicyanoheptafulvene (II)*

The values in (II) have been averaged over chemically equivalent bonds.



Bonds		
	(I)	(II)
<i>a</i>	1.311 Å	1.338 Å
<i>b</i>	1.448	1.415
<i>c</i>	1.353	1.339
<i>d</i>	1.425	1.465
<i>e</i>	1.422	1.361
<i>f</i>	1.450	1.417
<i>g</i>	1.125	1.137
Angles		
<i>k</i>	128.8°	126.2°
<i>l</i>	128.4	128.8
<i>m</i>	130.2	122.5
<i>n</i>	125.1	115.2
<i>o</i>	117.4	122.3
<i>p</i>	122.6	122.5
<i>q</i>	114.4	114.9
<i>r</i>	179.6	178.0

The bond lengths and angles expected to be chemically equivalent are essentially equal, as seen in Fig. 3. The corresponding values in (I) and (II) are compared in Table 6. The distortion of the bond angles in the seven-membered ring seems to be somewhat relieved by taking a boat form. The relief of strain may result in an increase of the *p* character and a concomitant elongation of the bond *a* (Table 6) (Dewar & Schmeising, 1960).

The marked changes in the bond lengths are observed in the bonds *d* and *e*. In the present compound the bond *d* is significantly longer and the exocyclic double bond *e* is considerably shorter than those in (I). The larger torsion angles of C(1)–C(7) and C(6)–C(7) inevitably cause a considerable reduction of the overlap of the *p* orbitals, and consequently the degree of the cross conjugation is decreased, resulting in the longer *d* and the shorter *e* in (II). These changes are accompanied satisfactorily by those in the bond angles *m* and *n*. Such features suggest that the contribution from the dipolar ionic structure (Ia) seems to be smaller in the present molecule (II) than in (I). In fact, the observed dipole moment of (II) is 5.68 D (Oda, 1967), while (I) has 7.5 D (Yamakawa, Watanabe, Mukai, Nozoe & Kubo, 1960; Cotton & Francis, 1960). The difference, 1.8 D, is too large to be attributed to the group moment of the two methyl groups.

No change is observed in the bond angles in the dicyanomethylene group between (I) and (II).

It is noted that the exocyclic double bond is bent downward to the bow plane, plane 2. Although the sense of bending is unfavourable for relieving the overcrowding, the overlap of the  $\pi$ -electrons between the seven-membered ring system and the dicyanomethylene group could be recovered to some extent by this bending. This can explain the fact that the exocyclic double bond is a little longer than the other double bonds. It also suggests the importance of  $\pi$  conjugation in the conformation of this system.

The C(1)–C(11) and C(6)–C(12) bond distances have typical  $C(sp^2)$ – $C(sp^3)$  values (Dewar & Schmeising, 1960).

The configuration of the C(7) and C(8) atoms is slightly pyramidal. The C(7) atom lies 0.035 Å above the plane of the adjacent carbon atoms, plane 6, while C(8) deviates 0.034 Å from plane 7 in the opposite sense. In spite of the intramolecular overcrowding, the deviations of C(1) and C(6) above the planes of the adjacent three carbon atoms are very small (planes 8 and 9 in Table 3). The greater deviations of C(7) and C(8), therefore, may be characteristic of the junction atoms in this cross-conjugated system.

Another view of the molecule is given in Fig. 4. The ring is folded about the long axis of the molecule. The dihedral angle between planes 4 and 5 is 131.9°.

As shown in Fig. 4, the molecular conformation has essentially mirror symmetry including the methyl hydrogen atoms. The H(11) and H(15) atoms are in the eclipsed conformation with C(2) and C(5) respectively, and consequently the intramolecular H(11)···H(2) and H(15)···H(5) distances are a little shorter than the sum of their van der Waals radii. It should be noted that in these conformations of the methyl groups the atoms H(12) and H(14) approach most closely to the cyano groups. The intramolecular C(9)···H(12) and C(10)···H(14) distances are somewhat shorter than the sum of their van der Waals radii. To examine the sterically preferred conformations, the methyl groups were artificially rotated at angular intervals of 10°. Several angular regions were found acceptable from the intramolecular and intermolecular contacts, but these were all different from the observed conformation. Therefore, the observed features should be interpreted by some attractive forces between the cyano groups and the methyl hydrogen atoms rather than intermolecular packing forces.

The thermal motions are best understood by looking at Fig. 5. The largest excursions are predictably those of the cyano nitrogens and one of the methyl groups, and are all in directions approximately perpendicular to the bonds linking them to the rest of the molecule.

In conclusion, it became apparent from the present structural investigation that resonance, steric and other effects must be taken into account in order to understand the structural features of the substituted 8,8-di-

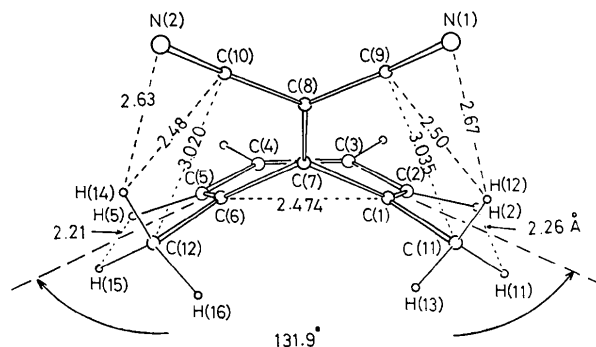


Fig. 4. Molecular conformation viewed along the vector between C(7) and the mid-point of C(3)–C(4).

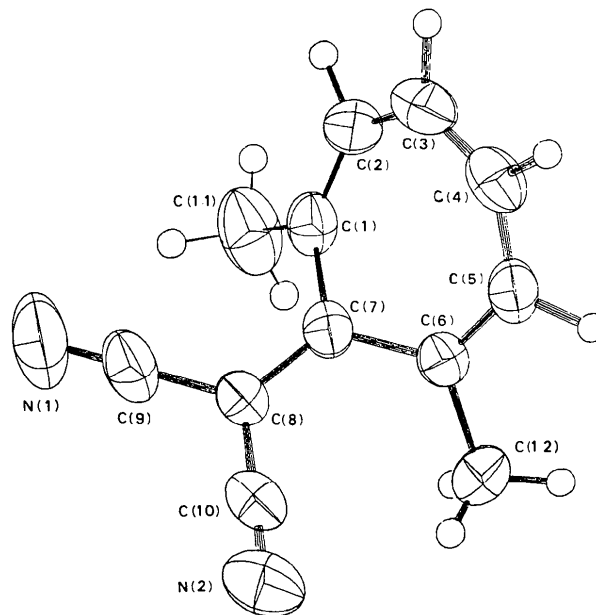


Fig. 5. Thermal ellipsoids at the 50% probability level. Hydrogen atoms are on an arbitrary scale.

cycanoheptafulvene. The introduction of the competing effects, the steric effect, illustrates the importance of the resonance effect in the 8,8-dicyanoheptafulvene system.

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## Structural Chemistry of the 8,8-Dicyanoheptafulvene System.

### III. The Crystal and Molecular Structure of 1-Isopropyl-8,8-dicyanoheptafulvene

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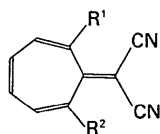
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1-Isopropyl-8,8-dicyanoheptafulvene,  $C_{13}H_{12}N_2$ , crystallizes in orange plates, space group  $P2_1/c$ , with dimensions  $a = 7.16$  (1),  $b = 13.26$  (1),  $c = 12.42$  (1) Å,  $\beta = 103.8$  (1)°, and  $Z = 4$ . The structure was solved by the symbolic addition method and refined by the full-matrix least-squares method. The final  $R$  value was 0.114. The seven-membered ring adopts a deep boat conformation, but lacks an exact  $m$  symmetry owing to the unsymmetrical intramolecular overcrowding effect.

#### Introduction

In the previous paper (Shimanouchi, Sasada, Kabuto & Kitahara, 1974), we showed that in the dicyanoheptafulvene system the ring conformation of the molecule is rather flexible, since the 1,6-dimethyl derivative (*Ib*) takes a deep boat form by the steric effects of substituted methyl groups.



- (I)  
 (a)  $R^1-R^2-H$   
 (b)  $R^1-R^2-CH_3$   
 (c)  $R^1-H, R^2-CH(CH_3)_2$

The present study of 1-isopropyl-8,8-dicyanoheptafulvene (*Ic*) was undertaken to examine the possible effects of the asymmetrical substitution on the conformation of the molecule.

#### Experimental

1-Isopropyl-8,8-dicyanoheptafulvene (1-isopropyl-8,8-dicyanomethylenecycloheptatriene) (*Ic*) crystallizes from a benzene-cyclohexane solution in the form of orange plates. The unit-cell dimensions were determined from zero-layer Weissenberg photographs about the  $b$  and  $c$  axes, calibrated with superimposed Al-powder lines. The crystal data are:  $C_{13}H_{12}N_2$ , M.W. 196.3, m.p. 81–82°C. Monoclinic,  $a = 7.16 \pm 0.01$ ,  $b = 13.26 \pm 0.01$ ,  $c = 12.42 \pm 0.01$  Å,  $\beta = 103.8 \pm 0.1^\circ$ ,  $U = 1145.1$  Å<sup>3</sup>,  $D_m = 1.13$  g cm<sup>-3</sup> (by flotation),  $D_x = 1.14$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 416$ ,  $\mu = 5.39$  cm<sup>-1</sup> (Cu  $K\alpha$ ). Ab-