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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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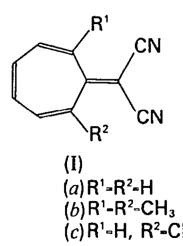
1-Isopropyl-8,8-dicyanoheptafulvene, $C_{13}H_{12}N_2$, crystallizes in orange plates, space group $P2_1/c$, with dimensions $a=7{\cdot}16$ (1), $b=13{\cdot}26$ (1), $c=12{\cdot}42$ (1) Å, $\beta=103{\cdot}8$ (1)°, and $Z=4$. The structure was solved by the symbolic addition method and refined by the 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 (I*b*) 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 (I*c*) 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) (I*c*) 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, $a=7{\cdot}16\pm0{\cdot}01$, $b=13{\cdot}26\pm0{\cdot}01$, $c=12{\cdot}42\pm0{\cdot}01$ Å, $\beta=103{\cdot}8\pm0{\cdot}1°$, $U=1145{\cdot}1$ Å^3, $D_m=1{\cdot}13$ g cm^{-3} (by flotation), $D_x=1{\cdot}14$ g cm^{-3}, $Z=4$, $F(000)=416$, $\mu=5{\cdot}39$ cm^{-1} (Cu $K\alpha$). Absent spectra, $0k0$ when k is odd and $h0l$ when l is odd.

The intensity data were collected from equi-inclination Weissenberg photographs at room temperature for the layer lines from 0 to 9 about the b axis and from 0 to 8 about the c axis, using Cu $K\alpha$ radiation. The cross sections of the crystals used, perpendicular to the rotation axes, were $0{\cdot}2 \times 0{\cdot}2$ mm for the b axis and $0{\cdot}3 \times 0{\cdot}25$ mm for the c axis. The intensities were estimated by visual comparison with a standard scale prepared with the same crystal. Out of 2290 independent reflexions recorded (about 83·4% of the Cu $K\alpha$ sphere), 908 were too weak to be measured. Corrections for Lorentz and polarization effects were made as usual and those for the spot-size variation in the high-layer photographs by the method of Phillips (1954). The correction for absorption was omitted.

Structure determination

The crystal structure was solved by the symbolic addition procedure (Karle & Karle, 1966), using the program *SORTE* (Nakatsu, 1967). The E map synthesized with 427 reflexions showed all the non-hydrogen atoms as the prominent peaks. The structure was refined by the block-diagonal matrix least-squares method. When the R value reached 0·156 using anisotropic temperature factors, a difference synthesis was calculated with the reflexions with $\sin\theta/\lambda \le 0{\cdot}45$. This revealed all the hydrogen atoms, and we concluded that the methyl groups do not rotate in the crystal. All the hydrogen atoms were then included in further full-matrix least-squares refinements; the positions and the individual isotropic temperature factors of the hydrogen atoms were allowed to shift, the seven strong reflexions affected by secondary extinction being excluded. The R value was 0·114 for the observed reflexions without the seven strong reflexions. When these were included, $R=0{\cdot}117$. The weighting scheme was $w=[1+0{\cdot}285(|F_o|-19)]^{-1}$ for $|F_o|>19{\cdot}0$, $w=1{\cdot}0$ for $|F_o|\le 19{\cdot}0$ and $w=0$ for the unobserved reflexions. The atomic scattering

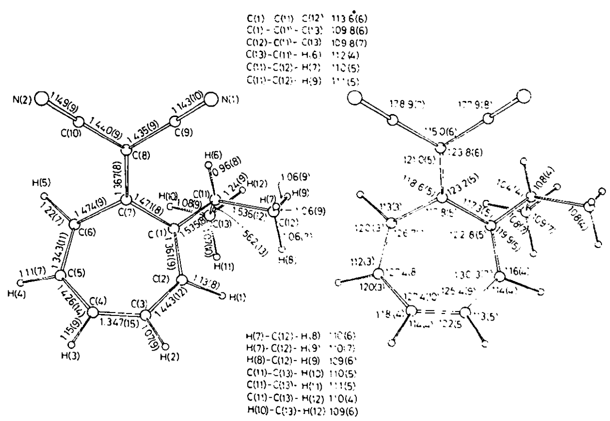


Fig. 1. Bond distances (Å) and angles (°). The corresponding e.s.d.'s, given in parentheses, refer to the last decimal positions.

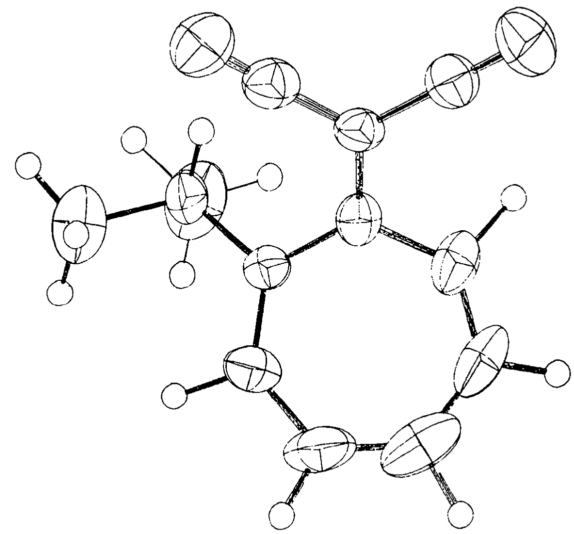


Fig. 2. Thermal ellipsoids of atoms drawn at the 50% probability level except for the hydrogen atoms.

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 $\times 10^5$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	8597 (10)	−25 (5)	6312 (5)	4126 (197)	704 (45)	1054 (57)	−216 (148)	1160 (169)	396 (85)
N(2)	5635 (9)	586 (5)	2913 (5)	3399 (171)	958 (52)	1070 (57)	−847 (152)	−557 (160)	−419 (87)
C(1)	9946 (7)	2634 (4)	5763 (4)	1760 (115)	438 (36)	600 (40)	256 (101)	334 (109)	−99 (61)
C(2)	9773 (10)	3557 (5)	6209 (5)	3113 (177)	499 (42)	772 (52)	124 (139)	802 (158)	−290 (75)
C(3)	8392 (13)	4351 (5)	5834 (8)	4402 (253)	510 (50)	1217 (80)	890 (179)	1867 (238)	−74 (97)
C(4)	7378 (11)	4486 (6)	4782 (9)	2523 (183)	695 (57)	1883 (115)	813 (164)	1998 (238)	746 (134)
C(5)	7437 (9)	3885 (6)	3839 (7)	1719 (134)	809 (59)	1155 (72)	238 (138)	135 (156)	979 (108)
C(6)	7919 (8)	2907 (5)	3826 (6)	1646 (125)	725 (52)	834 (55)	−57 (120)	−74 (129)	403 (81)
C(7)	8534 (7)	2239 (4)	4794 (4)	1267 (101)	563 (41)	595 (41)	5 (102)	288 (104)	27 (62)
C(8)	7919 (7)	1260 (4)	4707 (5)	1538 (110)	405 (36)	717 (45)	−54 (100)	236 (112)	−209 (62)
C(9)	8322 (9)	555 (5)	5611 (6)	2241 (147)	534 (44)	889 (57)	−187 (126)	587 (144)	−145 (83)
C(10)	6655 (9)	891 (5)	3703 (5)	2067 (137)	608 (46)	847 (54)	−159 (124)	82 (144)	−149 (78)
C(11)	11717 (8)	1978 (5)	6241 (5)	2206 (138)	539 (44)	571 (45)	−87 (120)	−344 (125)	−0 (66)
C(12)	12282 (12)	1955 (8)	7515 (6)	2736 (195)	1141 (77)	852 (65)	−116 (202)	450 (181)	467 (110)
C(13)	13458 (12)	2349 (8)	5791 (8)	2906 (198)	1221 (87)	1027 (73)	779 (211)	1390 (193)	561 (126)

Table 1 (*cont.*)

(*b*) Hydrogen atoms

Positional parameters are $\times 10^3$.

	x	y	z	B(Å^2)
H(1)	1084 (11)	373 (6)	702 (7)	5·1 (1·8)
H(2)	821 (11)	484 (7)	649 (7)	5·7 (2·0)
H(3)	626 (12)	512 (6)	467 (6)	5·9 (2·0)
H(4)	709 (9)	422 (5)	299 (5)	2·8 (1·4)
H(5)	800 (9)	250 (5)	296 (5)	3·4 (1·5)
H(6)	1131 (10)	131 (6)	599 (6)	3·6 (1·7)
H(7)	1104 (12)	182 (6)	782 (7)	5·2 (1·9)
H(8)	1287 (10)	266 (6)	779 (6)	3·4 (1·6)
H(9)	1332 (12)	138 (6)	780 (7)	5·0 (1·9)
H(10)	1310 (11)	233 (6)	490 (7)	5·2 (1·9)
H(11)	1385 (13)	310 (8)	605 (7)	6·3 (2·5)
H(12)	1486 (12)	179 (6)	614 (7)	5·5 (1·9)

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 with their standard deviations.*

* The structure-factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30334 (10pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

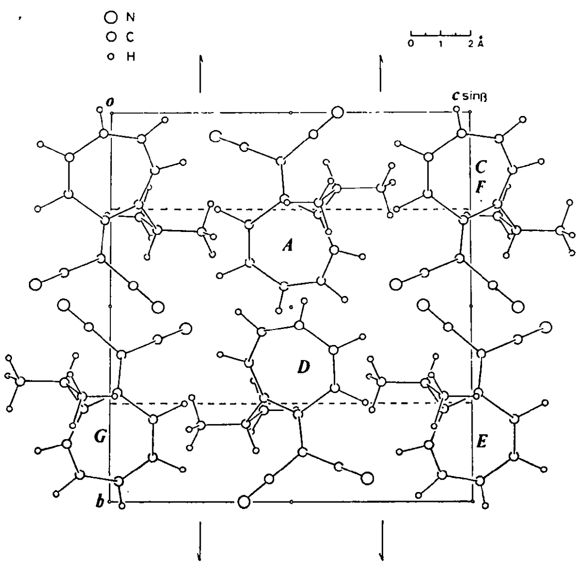


Fig. 3. Crystal structure viewed along the *a* axis.

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

Results and discussion

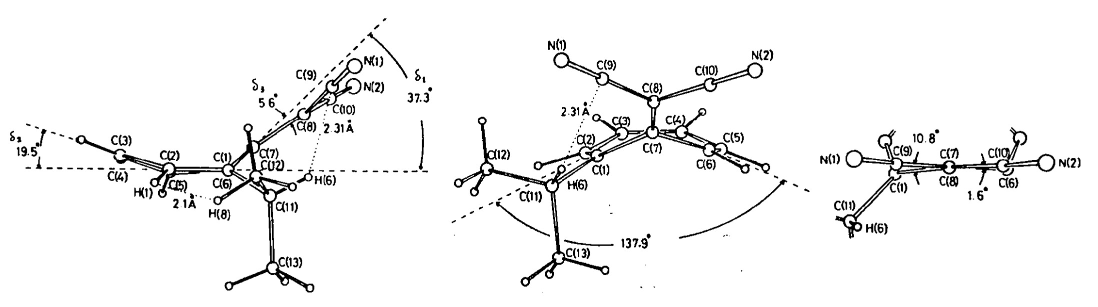
The bond lengths and angles are given in Fig. 1. Figs. 2 and 3 show the thermal ellipsoids of the atoms and the crystal structure viewed along the *a* axis. Short intermolecular distances are listed in Table 2. There are no abnormally short contacts; so it is unnecessary

Table 2. *Short intermolecular distances*

Atom in position *A*	Atom in position		Distance (Å)
Between heavy atoms shorter than 3·5 Å.			
N(1)	C(8)	*B*	3·466
C(9)	C(9)	*B*	3·462
Between heavy and hydrogen atoms shorter than 3·0 Å.			
N(1)	H(4)	*C*	2·78
H(2)	N(2)	*C*	2·90
H(7)	C(6)	*C*	2·83
C(4)	H(3)	*D*	2·89
H(1)	N(1)	*E*	2·60
H(9)	C(5)	*F*	2·94
H(11)	N(2)	*F*	2·93
N(2)	H(9)	*B*	2·91
H(4)	N(2)	*G*	2·70
Between hydrogen atoms shorter than 2·5 Å.			
H(7)	H(5)	*C*	2·40
H(3)	H(3)	*D*	2·17

Position*	General coordinates
A	$x, \quad y, \quad z$
B	$2-x, \quad \bar{y}, \quad 1-z$
C	$x, \quad \frac{1}{2}-y, \quad \frac{1}{2}+z$
D	$1-x, \quad 1-y, \quad 1-z$
E	$2-x, \quad \frac{1}{2}+y, \quad \frac{3}{2}-z$
F	$1+x, \quad \frac{1}{2}-y, \quad \frac{1}{2}+z$
G	$1-x, \quad \frac{1}{2}+y, \quad \frac{1}{2}-z$

* These are also indicated in Fig. 3.



(*a*) (*b*) (*c*)

Fig. 4. Molecular conformation (*a*) viewed along the line C(1)···C(6); (*b*) viewed along the vector between C(7) and the midpoint of C(3)–C(4). (*c*) Torsion angles about the exocyclic double bond.

to consider any serious effects of them on the molecular conformation.

The seven-membered ring in the present molecule also adopts a deep boat form, as shown in Fig. 4(*a*). The angle δ_1 is 37·3° and δ_2 19·5°, the definition of δ_1 and δ_2 being given in Table 5 in the preceding paper (Shimanouchi, Sasada, Kabuto & Kitahara, 1974). δ_1 is considerably smaller than the corresponding angle in (I*b*). This also suggests that there is a tendency to preserve the planarity in (I*a*). The degree of bond alternation in the seven-membered ring is essentially equal to that in (I*b*), which is discussed in detail in the preceding paper.

The torsion angles in the ring are listed in Table 3. The largest torsion angle is observed in the C(1)–C(7) bond. Even the double bond, C(1)–C(2), has a significant torsion angle of 5·5°. The bond-length difference between C(1)–C(2) and C(5)–C(6) may be attributable to this torsion. With regard to the torsion angles, there is no mirror symmetry passing through C(7), C(8) and the mid-point of the C(3)–C(4) bond, which seems to be the consequence of the intramolecular steric effect of the isopropyl group.

The effect of the intramolecular overcrowding is also seen in the values for some bond angles; C(1)–C(7)–C(8) is 123·2° while C(6)–C(7)–C(8) is 118·6° and C(7)–C(8)–C(9) is 123·8° while C(7)–C(8)–C(10) is 121·0°. Although the exocyclic angles at C(1) appear to contradict this, it has been pointed out that the bond angles about a trigonal carbon atom ($R^1R^2C{=}X$) are far from being equal and the smallest is almost always the angle opposite the double bond (*i.e.* $\angle R^1\text{–}C\text{–}R^2$) (Ammon & Plastas, 1971). Therefore the observed C(7)–C(1)–C(11) angle (117·3°) should be considered to increase from the usual value (about 115°) (Bordner, Parker & Stanford, 1972) by steric repulsion.

Another view of the molecule is given in Fig. 4(*b*). The dihedral angle between planes 4 and 5 in Table 4 is 137·9°, which is larger than the corresponding angle in (I*b*).

The intramolecular approach of H(6) to C(9) is examined in detail. The present feature is different from that observed in (I*b*) and the C(9)–N(1) bond is caught in a depression between the C(11)–C(12) and C(11)–H(6) bonds, as a result of the *gauche* conformation of the isopropyl group to the seven-membered

Table 3. *Torsion angles in the seven-membered ring*

C(7) [C(1) C(2)] C(3)	5·5°
C(1) [C(2) C(3)] C(4)	23·5
C(2) [C(3) C(4)] C(5)	0·5
C(6) [C(5) C(4)] C(3)	−25·9
C(7) [C(6) C(5)] C(4)	1·2
C(1) [C(7) C(6)] C(5)	44·7
C(6) [C(7) C(1)] C(2)	−47·8
C(8) [C(7) C(1)] C(2)	138·9
C(8) [C(7) C(6)] C(5)	−141·7

Table 4. *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
l	−0·9171	−0·8589	−0·7937	−0·7173	−0·9610	−0·9061	−0·8809
m	−0·2825	0·3472	−0·5810	−0·3747	−0·2648	0·2942	0·2881
n	0·2814	0·3766	0·1804	0·5875	−0·0799	0·3042	0·3756
p	3·973	0·820	5·482	1·088	5·753	1·617	1·152

Deviations of atoms (Å)

1		2		3		4		5		6		7	
C(1)	−0·022*	C(1)	0·000*	C(2)	−0·001*	C(1)	−0·020*	C(4)	0·002*	C(7)	0·000*	C(1)	0·000*
C(2)	0·019*	C(6)	0·000*	C(3)	0·002*	C(2)	0·021*	C(5)	−0·005*	C(9)	0·000*	C(6)	0·000*
C(5)	−0·019*	C(7)	0·000*	C(4)	−0·002*	C(3)	−0·010*	C(6)	0·005*	C(10)	0·000*	C(8)	0·000*
C(6)	0·023*			C(5)	0·001*	C(7)	0·009*	C(7)	−0·002*				
		C(2)	0·848							N(1)	0·041	C(2)	0·781
N(1)	2·195	C(5)	0·756	C(1)	0·410	C(4)	−0·525	C(1)	−0·930	N(2)	0·041	C(5)	0·687
N(2)	1·834	C(8)	−0·134	C(6)	0·475	C(6)	−0·899	C(3)	−0·450	C(1)	−0·147	C(7)	0·048
C(3)	0·398	C(9)	−0·066			C(11)	−0·163	C(8)	0·749	C(6)	0·045	C(9)	0·122
C(4)	0·371	C(10)	−0·238							C(8)	−0·038	C(10)	−0·061
C(7)	0·461	N(1)	−0·005									C(11)	−1·026
C(8)	1·178	N(2)	−0·311										
C(9)	1·730												
C(10)	1·533												
C(11)	−0·647												
C(12)	−0·231												
C(13)	−2·205												

Interplanar angles (°)

Plane	2	3	4	5	6	7
1	37·3	19·5	21·7	21·0	33·5	33·7
2		56·8	45·0	45·3	5·8	3·6
3			26·8	25·6	52·9	53·2
4				42·1	44·1	41·9
5					39·8	42·3
6						4·4

ring atoms. The intramolecular H(1)···H(8) contact is 2·1 Å.

The torsion angle about the exocyclic double bond can be seen in Fig. 4(*c*). A larger torsion is observed in C(9)–C(8)–C(7)–C(1). The sense of the torsion is compatible with the repulsion between a cyano and the isopropyl group. The C(8) atom lies 0·038 Å above the plane of the adjacent carbon atoms, plane 6 in Table 5, while the C(7) atom deviates 0·048 Å from plane 7 in the opposite sense. The exocyclic double bond is bent downward to the bow plane, as is that in (I*b*).

The combined effect of the deviation from planarity, the bond-angle distortions and the slight torsion of the double bonds lead to the minimum non-bonded C···H distance of 2·31 Å [C(9)···H(6)]. In connexion with the low-field shift of the methine proton [H(6)] signals ($\delta = 3{\cdot}35$ p.p.m. in acetonitrile at room temperature) in the n.m.r. spectrum, this C···H approach may provide some information about the magnetic anisotropy of the cyano group (Shimanouchi, 1964). The methyl groups all have the usual staggered conformation.

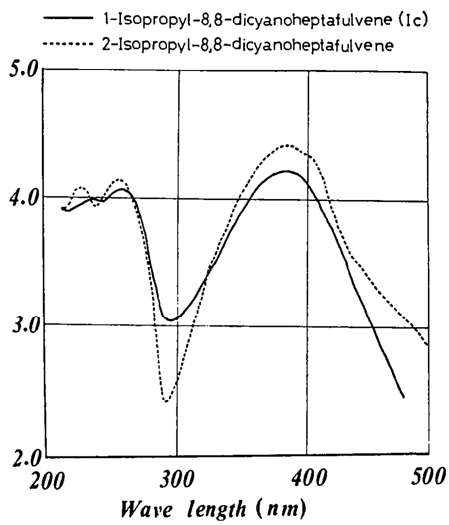


Fig. 5. Ultraviolet absorption spectra in methanol.

It is well known that the molecular distortion caused by overcrowding has a pronounced effect upon the UV absorption spectrum in certain aromatic systems. The effect is characterized by bathochromic and hyperchromic displacements of the longer wave-length maxima, and a diminution of fine structure in these regions (Mosby, 1953). In the present molecule no bathochromic shift is evident and hypochromic displacement is observed in the longer wave-length region as shown in Fig. 5, which shows the non-planarity of this version of the non-benzenoid aromatic system.

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