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*Acta Cryst.* (1995). **C51**, 1397–1399

# Dimethyl 4-*exo*,9-*endo*-Dibromobicyclo[3.3.1]non-2-ene-2,3-dicarboxylate

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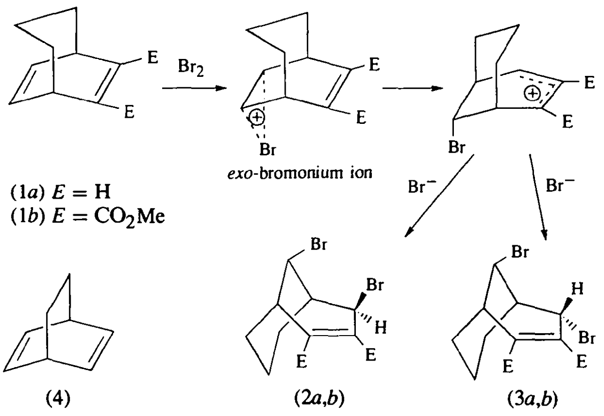
(*Received* 8 *August* 1994; *accepted* 25 *January* 1995)

## Abstract

The bromination reaction of dimethyl bicyclo[3.2.2]nona-6,8-diene-6,7-dicarboxylate, (1*b*), gave the title compound (2*b*), $C_{13}H_{16}Br_2O_4$, and dimethyl 4-*exo*,9-*exo*-dibromobicyclo[3.3.1]non-2-ene-2,3-dicarboxylate, (3*b*). The saturated six-membered ring of (2*b*) adopts a chair conformation with the Br atom in an equatorial position.

## Comment

The electrophilic bromination reaction of norbornadiene, which gave the skeleton-rearranged dibromide, is of interest in connection with the intramolecular mutual interaction of the two double bonds (Winstein & Shatavsky, 1956; Schmerling, Luvisi & Welch, 1956). On the other hand, in the case of the norbornadiene homologues, bicyclodienes (1*a*) and (4), 1,5- and 1,2-addition, under similar conditions, of the bromine to the common cyclohexa-1,4-diene part in the molecule occurred to give dibromides without any skeleton-rearrangement products (Fickes & Metzs, 1978; Gagneux & Grob, 1959; Grob & Hostynek, 1963). Regarding the synthetic work for the norbornadiene homologues bicyclo[4.2.2]deca-7,9-diene and bicyclo[5.2.2]undeca-8,10-diene (Satake, Usumoto, Hikasa, Kimura, Kishima & Morosawa, 1992), a reinvestigation of the bromination reaction of the bicyclodiene (1*a*) and its dimethoxycarbonyl derivative (1*b*) was undertaken in order to investigate a systematic change in features of the mutual intramolecular interactions of the 1,4-cyclohexadiene part of the structure.



When equimolar bromine was added to a dichloromethane solution of bicyclodiene (1*a*) or (1*b*) at 273 K, a hitherto unknown skeletal rearrangement occurred in both cases to give mixtures of dibromides presumably *via* an *exo*-bromonium ion of the starting bicyclodiene. The mixtures were chromatographed independently on silica gel and gave 9-*endo*- and 9-*exo*-dibromides (2*a*) and (3*a*), and (2*b*) and (3*b*), respectively. On the basis of $^1H$ and $^{13}C$ NMR spectra, these dibromides were shown to have the same carbon skeleton. We report here the structure of (2*b*) (Fig. 1).

The structure reported here is the first example of an X-ray structural analysis of the bicyclo[3.3.1]non-2-ene system. The features of the bicyclic ring are summarized as a chair-form cyclohexane ring [C(1)—C(9)—C(5)—C(6)—C(7)—C(8)] and a bending cyclohexene ring [C(1)—C(2)—C(3)—C(4)—C(5)—C(9)] whose five C

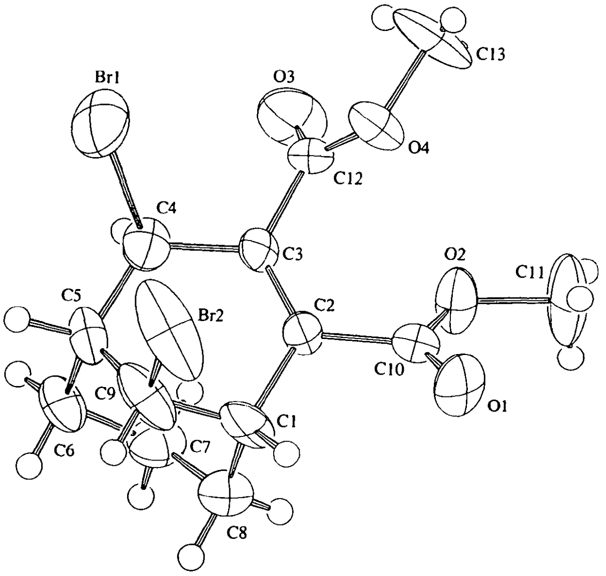


Fig. 1. *ORTEP*II diagram (Johnson, 1976) of the title compound with displacement ellipsoids of 50% probability drawn for non-H atoms. H atoms are represented as spheres equivalent to $B = 1.0$ Å$^2$.

atoms, C(1)—C(5), are arranged in a coplanar configuration [C(1)—C(2)—C(3)—C(4) −2 (1) and C(2)—C(3)—C(4)—C(5) 5 (1)°]. The dihedral angle between the plane defined by C(1), C(9) and C(1), and that through C(2), C(3), C(4) and C(5) is 127.1 (9)°, while the corresponding angle for unsubstituted bicyclo[3.3.1]non-2-ene is estimated to be 123° by MM2 calculations (Allinger, 1977). A larger dihedral angle for compound (2*b*) is attributable to the intramolecular steric repulsion between Br atoms [Br(1)···Br(2) 3.677 (1) Å].

## Experimental

Crystals of (2*b*) were grown by slow evaporation from a dichloromethane solution.

### *Crystal data*

$C_{13}H_{16}Br_2O_4$
$M_r = 396.1$
Orthorhombic
*Pbca*
$a = 13.945\ (9)$ Å
$b = 15.406\ (8)$ Å
$c = 13.830\ (8)$ Å
$V = 2971\ (3)$ Å$^3$
$Z = 8$
$D_x = 1.771$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}11°$
$\mu = 5.41$ mm$^{-1}$
$T = 295$ K
Prismatic
0.38 × 0.30 × 0.25 mm
Colourless

### *Data collection*

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan
$T_{\min} = 0.85$, $T_{\max} = 1.00$
2942 measured reflections
2641 independent reflections
1141 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.031$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 18$
$l = -1 \rightarrow 16$
3 standard reflections monitored every 97 reflections intensity decay: 2.7%

### *Refinement*

Refinement on *F*
$R = 0.047$
$wR = 0.030$
$S = 1.53$
1141 reflections
237 parameters
All H-atom parameters refined isotropically
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.63$

$\Delta\rho_{\max} = 0.73$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.73$ e Å$^{-3}$
Extinction correction: $I_{\rm corr} = I_o(1 + gI_c)$
Extinction coefficient: $2.12 \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| Br(1) | 0.48704 (7) | 0.01680 (8) | 0.13032 (7) | 7.72 (7) |
| Br(2) | 0.40333 (6) | −0.20945 (8) | 0.13611 (8) | 8.58 (7) |
| O(1) | 0.2800 (4) | −0.1960 (4) | 0.4276 (4) | 4.9 (4) |
| O(2) | 0.3361 (4) | −0.0718 (4) | 0.4902 (4) | 4.6 (3) |
| O(3) | 0.4396 (4) | 0.0938 (4) | 0.3633 (5) | 6.2 (4) |
| O(4) | 0.3005 (4) | 0.0296 (4) | 0.3226 (4) | 4.0 (3) |
| C(1) | 0.4677 (7) | −0.2132 (6) | 0.3334 (8) | 4.2 (6) |
| C(2) | 0.4168 (5) | −0.1290 (6) | 0.3556 (6) | 2.6 (4) |
| C(3) | 0.4409 (5) | −0.0538 (6) | 0.3161 (6) | 2.5 (4) |
| C(4) | 0.5253 (6) | −0.0478 (6) | 0.2478 (6) | 3.7 (5) |
| C(5) | 0.5745 (6) | −0.1327 (7) | 0.2221 (6) | 3.7 (6) |
| C(6) | 0.6603 (7) | −0.1502 (8) | 0.2892 (7) | 4.0 (6) |
| C(7) | 0.6299 (8) | −0.1608 (7) | 0.3932 (7) | 4.2 (6) |
| C(8) | 0.5523 (8) | −0.2298 (8) | 0.4031 (9) | 5.2 (7) |
| C(9) | 0.5085 (7) | −0.2100 (7) | 0.2307 (7) | 5.2 (6) |
| C(10) | 0.3347 (6) | −0.1374 (6) | 0.4279 (6) | 2.9 (5) |
| C(11) | 0.254 (1) | −0.071 (1) | 0.558 (1) | 8 (1) |
| C(12) | 0.3945 (7) | 0.0321 (6) | 0.3372 (6) | 3.2 (5) |
| C(13) | 0.251 (1) | 0.111 (1) | 0.348 (2) | 7 (1) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Br(1)—C(4) | 1.979 (8) | C(1)—C(9) | 1.53 (1) |
| Br(2)—C(9) | 1.965 (9) | C(2)—C(3) | 1.325 (9) |
| O(1)—C(10) | 1.183 (8) | C(2)—C(10) | 1.52 (1) |
| O(2)—C(10) | 1.328 (9) | C(3)—C(4) | 1.51 (1) |
| O(2)—C(11) | 1.48 (1) | C(3)—C(12) | 1.50 (1) |
| O(3)—C(12) | 1.196 (9) | C(4)—C(5) | 1.52 (1) |
| O(4)—C(12) | 1.327 (9) | C(5)—C(6) | 1.54 (1) |
| O(4)—C(13) | 1.48 (1) | C(5)—C(9) | 1.51 (1) |
| C(1)—C(2) | 1.51 (1) | C(6)—C(7) | 1.51 (1) |
| C(1)—C(8) | 1.54 (1) | C(7)—C(8) | 1.52 (1) |
| C(10)—O(2)—C(11) | 114 (1) | C(4)—C(5)—C(9) | 112.6 (8) |
| C(12)—O(4)—C(13) | 113.8 (8) | C(6)—C(5)—C(9) | 106.8 (8) |
| C(2)—C(1)—C(8) | 111.9 (9) | C(5)—C(6)—C(7) | 112.1 (8) |
| C(2)—C(1)—C(9) | 109.6 (9) | C(6)—C(7)—C(8) | 111.2 (9) |
| C(8)—C(1)—C(9) | 107.5 (8) | C(1)—C(8)—C(7) | 111.8 (9) |
| C(1)—C(2)—C(3) | 123.3 (8) | Br(2)—C(9)—C(1) | 109.9 (7) |
| C(1)—C(2)—C(10) | 114.8 (8) | Br(2)—C(9)—C(5) | 113.6 (7) |
| C(3)—C(2)—C(10) | 122.3 (8) | C(1)—C(9)—C(5) | 109.0 (8) |
| C(2)—C(3)—C(4) | 120.5 (8) | O(1)—C(10)—O(2) | 126.3 (9) |
| C(2)—C(3)—C(12) | 125.6 (7) | O(1)—C(10)—C(2) | 123.2 (9) |
| C(4)—C(3)—C(12) | 113.8 (8) | O(2)—C(10)—C(2) | 110.5 (8) |
| Br(1)—C(4)—C(3) | 109.5 (6) | O(3)—C(12)—O(4) | 126.1 (9) |
| Br(1)—C(4)—C(5) | 111.3 (6) | O(3)—C(12)—C(3) | 122.2 (9) |
| C(3)—C(4)—C(5) | 116.5 (5) | O(4)—C(12)—C(3) | 111.7 (8) |
| C(4)—C(5)—C(6) | 111.2 (8) | | |
| C(1)—C(2)—C(3)—C(4) | −2 (1) | C(7)—C(8)—C(1)—C(9) | 57 (1) |
| C(1)—C(9)—C(5)—C(4) | −56 (1) | Br(1)—C(4)—C(3)—C(2) | 131.8 (7) |
| C(2)—C(1)—C(9)—C(5) | 57 (1) | C(3)—C(4)—C(5)—C(9) | 26 (1) |
| C(2)—C(3)—C(4)—C(5) | 5 (1) | C(1)—C(8)—C(7)—C(6) | −52 (1) |
| C(3)—C(2)—C(1)—C(9) | −29 (1) | C(1)—C(9)—C(5)—C(6) | 66 (1) |
| C(5)—C(6)—C(7)—C(8) | 54 (1) | Br(2)—C(9)—C(5)—C(4) | 66.4 (9) |
| C(5)—C(9)—C(1)—C(8) | −65 (1) | C(4)—C(3)—C(2)—C(10) | 177.5 (7) |
| C(7)—C(6)—C(5)—C(9) | −60 (1) | C(1)—C(2)—C(3)—C(12) | −178.4 (8) |

Data collection and cell refinement were carried out with *MSC/AFC Data Collection and Refinement Software* (Rigaku Corporation, 1990). The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) and refined by full-matrix least squares using *TEXSAN* (Molecular Structure Corporation, 1985). The displacement ellipsoids were drawn with the aid of *ORTEP*II (Johnson, 1976). The calculations were performed on a VAX 3100 computer using *TEXSAN* at the X-ray Laboratory of Okayama University.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AS1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). C**51**, 1399–1401

# 1,2-Dicyanobenzene. A Precursor of Phthalocyanines

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(*Received* 18 *November* 1994; *accepted* 27 *January* 1995)

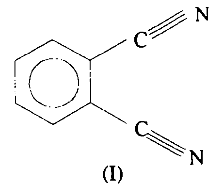
## Abstract

The molecule of 1,2-dicyanobenzene, $C_8H_4N_2$, possesses mirror symmetry. The two cyano groups are bent slightly above the plane of the molecule. The six aromatic C—C bonds in the benzene ring have a mean value of 1.377 Å. The C—CN and $C\equiv N$ bond lengths are 1.430 (7) and 1.149 (8) Å, respectively. The internal angles in the benzene ring differ slightly from 120°. The shortest intermolecular contact is N(1)···H(2) of 2.657 (16) Å.

## Comment

We have used 1,2-dicyanobenzene as a precursor in the synthesis of phthalocyanines. Using a previously described preparation method (Kubiak & Janczak, 1993), we obtained several metallophthalocyanines (Janczak & Kubiak, 1993*a*,*b*, 1994*a*) and a new group of compounds, the bicyclic phthalocyanines (Janczak & Kubiak, 1994*b*).

Of the three isomers of dicyanobenzene, only the crystal structure of the 1,4-isomer has been published (Van Rij & Britton, 1977; Drück & Littke, 1978; Colapietro, Domenicano, Portalone, Schultz & Hargittai, 1984). This paper reports the crystal structure of the 1,2-isomer, (I).



(I)

The molecular geometry with the atomic numbering is shown in Fig. 1. The crystals are composed of isolated molecules of 1,2-dicyanobenzene. The two cyano groups are slightly bent above the benzene plane retaining molecular symmetry *m*. This plane is perpendicular to the benzene ring and bisects the C(1)—C($1^{\rm i}$) and C(3)—C($3^{\rm i}$) bonds [symmetry code: (i) $-x, y, z$]. The mean aromatic C—C bond length of 1.377 Å is comparable to analogous mean distances found in the 1,4-isomer (1.388 Å; Drück & Littke, 1978) and in 1,2,4,5-tetracyanobenzene [1.401 (8) Å; Prout & Tickle, 1978]. The $C\equiv N$ bond length of 1.149 (8) Å is typical of cyano groups and comparable to C—N distances found in various cyano derivatives (Britton, 1981*a*,*b*; Casado, Nygaard & Sorensen, 1971; Colapietro, Domenicano, Marciante & Portalone, 1981). The C—CN distance of 1.430 (7) Å is comparable to C—CN distances of 1.451 (13) Å in the 1,4-isomer (Drück & Littke, 1978), 1.446 (8) Å in 1,2,4,5-tetracyanobenzene (Prout & Tickle, 1978) and 1.439 (6) Å in 4-cyanopyridine (Laing, Sparrow & Sommerville, 1971). This bond length is intermediate between the expected value of 1.419 Å for $sp$–$sp^2$ C—C bond lengths and the value of 1.459 Å for $sp$–$sp^3$ C—C bond lengths (Stoecheff, 1962).

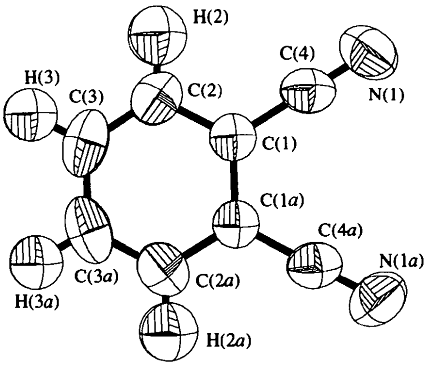


Fig. 1. View of the molecular structure of 1,2-dicyanobenzene with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

The mutual arrangement of the 1,2-dicyanobenzene molecules is illustrated in Fig. 2. The structure is composed of linear stacks of parallel and overlapping molecules forming a quasi-herringbone bond array. The distance between two successive parallel benzene rings is 3.503 (14) Å. This value is a little larger than the

*Acta Crystallographica Section C*
ISSN 0108-2701 ©1995