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# The Crystal and Molecular Structures of Paracyclophadiynes

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The molecular structures of tetramethyl[3.3]paracyclophadine(I) and [3.4]paracyclophadiyne(II) have been determined by X-ray analysis. Both crystals are monoclinic, with the space group of $P2_1/c$. The crystal data are: $a=9.170(4)$, $b=9.208(3)$, $c=18.232(7)$ Å, $\beta=94.0(1)°$, $Z=4$ for (I) and $a=10.938(3)$, $b=9.173(2)$, $c=14.988(4)$ Å, $\beta=116.1(1)°$, $Z=4$ for (II). In both molecules, consisting of benzene and diacetylene groups linked by two methylene-bridges, the diacetylene chain is bent into a bow shape. The (I) molecule has Cs symmetry, and the distances (3.019—3.256 Å) between the atoms of the diacetylene group and the benzene plane are smaller than those of [3.3]paracyclophadiyne(Aono, Sakabe, Sakabe, Katayama, and Tanaka, 1975). The methylene-bridge of [3.4]paracyclophadiyne has a disordered structure.

Misumi and his collaborators1) have synthesized a series of paracyclophadiyne derivatives, and the chemical and spectral properties1–3) and the crystal structures4,5) have been investigated. We have ourselves now determined the structures of tetramethyl[3.3]-paracyclophadiyne(I) and [3.4]paracyclophadiyne(II) in order to study the interactions between the diacetylene group and the benzene ring in more detail.

## Experimental

The space group of the two colorless crystals were determined as $P2_1/c$ from the systematic absences on the oscillation and Weissenberg photographs. The unit-cell parameters were determined by the least-squares method, using twelve reflections measured on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation for (I) and Ni-filtered Cu $K\alpha$ radiation for (II). In order to confirm the stability of the crystal and counting systems, the intensities of three standard reflections were monitored after every 100 reflections. The standard reflections were stable within a 1% fluctuation in both crystals. Neither absorption nor extinction correction was made. The crystal data and their experimental conditions are shown in Table 1.

TABLE 1. CRYSTAL DATA AND EXPERIMENTAL CONDITIONS

| | Tetramethyl[3.3]-paracyclophadiyne | [3.4]Paracyclophadiyne |
|---|---|---|
| Molecular formula | $C_{20}H_{24}$ | $C_{17}H_{18}$ |
| Molecular weight | 264.4 | 222.3 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $a$ | 9.170(4) Å | 10.938(3) Å |
| $b$ | 9.208(3) Å | 9.173(2) Å |
| $c$ | 18.232(7) Å | 14.988(4) Å |
| $\beta$ | 94.0(1)° | 116.1(1)° |
| $V$ | 1535.7 Å$^3$ | 1350.5 Å$^3$ |
| $Z$ | 4 | 4 |
| $D_c$ | 1.143 g cm$^{-3}$ | 1.094 g cm$^{-3}$ |
| $\mu$ | 0.69 cm$^{-1}$ (for Mo $K\alpha$) | 4.66 cm$^{-1}$ (for Cu $K\alpha$) |
| Crystal size | 0.22×0.22×0.22 mm | 0.25×0.25×0.35 mm |
| Scan technique | $2\theta$-$\omega$ step scan | $2\theta$-$\omega$ step scan |
| Range ($\omega$) | 1.2° | 1.2° |
| Step | 0.02° | 0.02° |
| Counting time/step | 2 s | 2 s |
| Maximum $2\theta$ | 54° | 144° |

## Determination and Refinement of the Structure

*Tetramethyl[3.3]paracyclophadiyne.* The structure was determined by the direct method with the MULTAN program,12) using 188 reflections with $|E|\geqq 1.40$. An E map computed from the phase set with the highest figure of merit ($FOM=1.65$) revealed the locations of all the non-hydrogen atoms. The hydrogen atoms were found on a difference Fourier map computed after the refinement of the carbon atoms. The refinement was performed by the block-diagonal least-squares method with 1508 independent reflections of $|F_o|>3\sigma(F_o)$. The $R$ index converged to 0.058 with an equal weight for each reflection.

*[3.4]Paracyclophadiyne.* The unit-cell parameters and the relative magnitude of the structure factors are very similar to those of [3.3]paracyclophadiyne-(III);4) therefore, the two molecules seemed to take a similar structure in the crystals. All the non-hydrogen atoms were located on a Fourier map computed with the phases calculated for the crystal of (III), the structure was found to be disordered. The structure was refined by the block-diagonal least-squares method, with several different occupancies for the atoms of disordered trimethylene-bridge. The minimum $R$ value of 0.083 was obtained when the occupancy factors of 0.55 and 0.45 were assigned to C(8a) and C(8b) respectively, while the $R$ value calculated by the equal occupancy factors was 0.085. The hydrogen atoms of the aromatic ring and tetramethylene-bridge were found on a difference Fourier map after the anisotropic refinement for the non-hydrogen atoms, those of the disordered trimetylene-bridge were also located after the refinement of the other atoms. The refinement was carried out with an equal weight for 1504 independent reflections of $|F_o|\geqq 3\sigma(F_o)$.

The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography."13) The least-squares program used for the refinement was written by one of the present authors (C.K.). The

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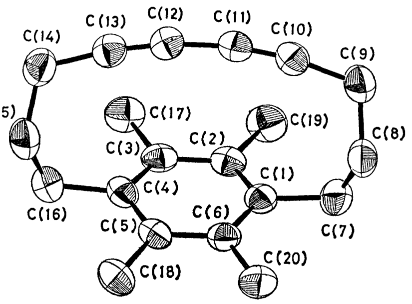

Fig. 1. The atomic numberings of tetramethyl[3.3]paracyclophdiyne.

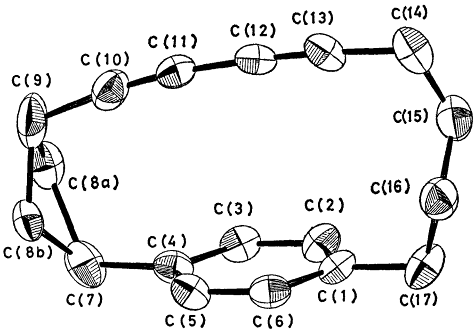

Fig. 2. The atomic numberings of [3.4]paracyclophadiyne.

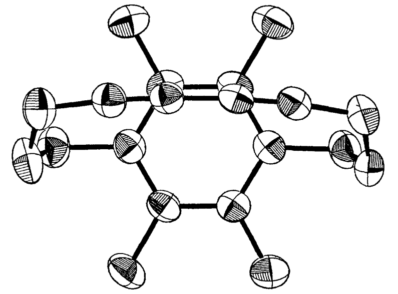

Fig. 3. The molecular structure of tetramethyl[3.3]-paracyclophadiyne projected onto the benzene ring.

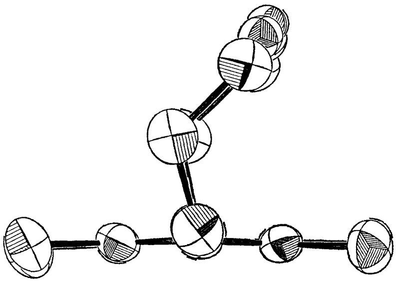

Fig. 4. The molecular structure of tetramethyl[3.3]-paracyclophadiyne viewed from the trimethylene bridge.

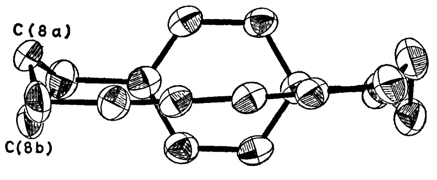

Fig. 5. The molecular structure of [3.4]paracyclophadiyne projected onto the benzene plane.

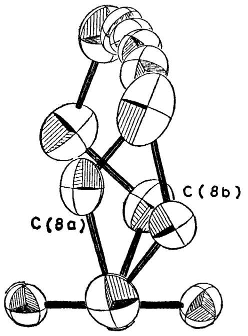

Fig. 6. The molecular structure of [3.4]paracyclophadiyne viewed from the disordered trimethylene bridge.

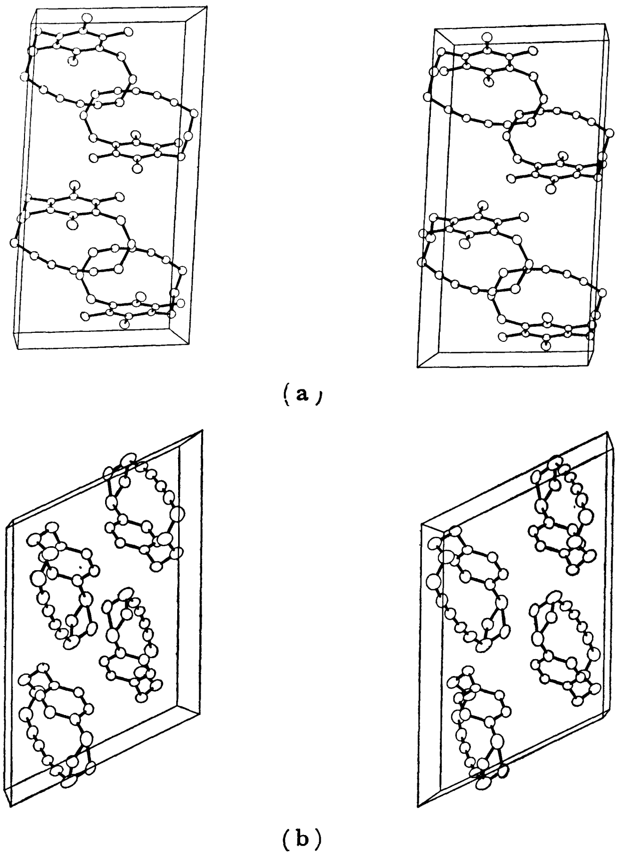

Fig. 7. The stereoscopic views of the crystals with the thermal ellipsoids as having 20% probability. For the origin at the lower rear right-hand corner, *a* is to the left, *b* is out, and *c* is up of the paper:
(a) tetramethyl[3.3]paracyclophadiyne,
(b) [3.4]paracyclophadiyne.

ORTEP program[14] was used for the drawing of Figs. 1—7. The computations were performed at the Nagoya University Computation Center and at Ube Industries. The observed and calculated structure factors are given in Tables 2 and 3.[15]

## Results and Discussion

The molecular structures, with atomic numbering, are shown in Figs. 1 and 2, where each atom is represented by a thermal ellipsoid as having a 50% probability for (I) and a 20% one for (II). The

Table 4. Final atomic coordinates and e.s.d.'s($\times 10^4$) for carbon atoms
The standard deviations are given in parentheses and refer to the last decimal position of the respective values.

| (I) | | | | (II) | | | |
|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | | $x$ | $y$ | $z$ |
| C (1) | 5870(4) | −239(4) | 3987(2) | C (1) | 2515(4) | −23(5) | 1714(3) |
| C (2) | 7237(4) | 415(4) | 3919(2) | C (2) | 3880(4) | −29(5) | 2405(3) |
| C (3) | 8519(4) | −387(4) | 4076(2) | C (3) | 4368(4) | 1031(5) | 3137(3) |
| C (4) | 8450(4) | −1833(4) | 4312(2) | C (4) | 3553(4) | 2107(5) | 3220(3) |
| C (5) | 7085(4) | −2444(4) | 4436(2) | C (5) | 2190(4) | 2102(5) | 2515(3) |
| C (6) | 5807(4) | −1651(4) | 4271(2) | C (6) | 1694(4) | 1067(5) | 1791(3) |
| C (7) | 4448(4) | 538(4) | 3738(2) | C (7) | 4104(5) | 3216(5) | 4052(4) |
| C (8) | 3708(4) | −19(5) | 3013(2) | C (8a) | 4376(8) | 2519(10) | 5196(6) |
| C (9) | 4413(4) | 409(5) | 2311(2) | C (8b) | 3334(10) | 3350(10) | 4600(7) |
| C (10) | 5806(4) | −336(4) | 2229(2) | C (9) | 3266(6) | 2082(7) | 5330(4) |
| C (11) | 6921(4) | −991(4) | 2258(2) | C (10) | 2653(5) | 675(6) | 4824(3) |
| C (12) | 8201(4) | −1762(4) | 2425(2) | C (11) | 2226(4) | −400(5) | 4361(3) |
| C (13) | 9245(4) | −2384(4) | 2680(2) | C (12) | 1797(4) | −1583(5) | 3745(3) |
| C (14) | 10440(4) | −3190(5) | 3065(2) | C (13) | 1471(4) | −2562(5) | 3196(4) |
| C (15) | 10071(5) | −3823(5) | 3792(2) | C (14) | 1152(6) | −3720(6) | 2465(5) |
| C (16) | 9829(4) | −2766(5) | 4424(2) | C (15) | 1770(6) | −3380(6) | 1797(4) |
| C (17) | 9990(4) | 313(5) | 3964(2) | C (16) | 995(5) | −2250(6) | 1059(3) |
| C (18) | 6984(5) | 3955(5) | 4762(2) | C (17) | 1972(5) | −1175(7) | 910(3) |
| C (19) | 7335(5) | 1974(4) | 3660(2) | | | | |
| C (20) | 4345(4) | −2347(5) | 4401(2) | | | | |

positional and thermal parameters of the non-hydrogen atoms are given in Tables 4 and 5.[15] The coordinates and isotropic thermal parameters of hydrogen atoms are given in Table 6.[15] The bond lengths and angles are listed in Tables 7 and 8 respectively.

*Molecular Structure of Tetramethyl[3.3]paracyclophadiyne.* The bond lengths in the benzene ring are 1.396—1.405 Å (mean 1.401 Å), somewhat longer than the value found for other paracyclophadiynes and close to those found for some cyclophanes[11] in which electron-donor-acceptor(EDA) interaction is considerable and for a complex of hexamethylbenzene with TCNE.[16] These results are reasonable, since some electrons in the bonding MO of the benzene ring are transfered to the vacant MO of the acceptor.

It has been reported that in the cyclophanes[6–11] and [3.3]paracyclophadiyne(III),[4] an angle of the carbon replaced by a methylene group is smaller by a few degree than the value of 120°, but the bond angles of C(2)–C(1)–C(6) and C(3)–C(4)–C(5) are very close to that of the normal $sp^2$ carbon. Therefore, it seems that the deformation of the benzene ring from the hexagonal shape is restricted by the repulsive forces between the methylene and methyl groups in the molecule. Although the substituent on the benzene ring has been reported to shrink the internal angle at the position of substitution,[17] the present molecule has substituent for all the atoms in the ring; therefore, the above effect might be cancelled.

The deviations of the atoms from the least-squares plane of the benzene ring are listed in Table 9. The C(1) and C(4) atoms in the ring deviate toward the diacetylene group, and the other atoms, C(2), C(3), C(5), and C(6), are displaced in the opposite direction. The deviations of the C(7) and C(16) atoms, which are the atoms of methylene groups substituted into the ring, are also displaced toward the diacetylene group. The dihedral angles between the least-squares plane composed of C(2), C(3), C(5), and C(6) and the planes through C(1), C(2), and C(6) and C(3), C(4), and C(5) are 4.3 and 4.0 °, respectively. The angles are greater than the value of 1.8° of (III).

A characteristic feature of the methyl groups attached to the benzene ring is the deviation from the benzene plane to the outer side of the molecule, not toward the center, as with the hydrogen of many paracyclophanes; this is perhaps due to the repulsion of the methyl and methylene groups. A similar displacement of the methyl group is found in tetramethyl quandruple-layered cyclophane.[10]

The bond lengths of the diacetylene group are almost the same as those of other paracyclophadiynes. The diacetylene chain is bent into a bow shape, which is characterized by the mean bond angle of 171.1° in the C(10), C(11), C(12), and C(13) atoms.

The molecular structures projected onto the benzene plane and from a trimethylene-bridge are shown in Figs. 3 and 4 respectively. The molecule has Cs symmetry, and the diacetylene group is nearly overlapped on the atoms of C(2) and C(3). The features of this molecules are distinct compared with those of (II) and (III), in which the diacetylene chaines are located on the mirror plane containing the C(1) and C(4) atoms.

It has been reported that the interaction between a methyl-substituted benzene and TCNE increases in

Table 7. Bond lengths ($l$/Å) and their standard deviations of nonhydrogen atoms

| | | | |
|---|---|---|---|
| (a) Tetramethyl[3.3]paracyclophadiyne | | | |
| C (1) -C (2) | 1.404(5) | C (1) -C (6) | 1.402(5) |
| C (1) -C (7) | 1.529(6) | C (2) -C (3) | 1.400(5) |
| C (2) -C (19) | 1.516(6) | C (3) -C (4) | 1.403(5) |
| C (3) -C (17) | 1.522(6) | C (4) -C (5) | 1.405(5) |
| C (4) -C (16) | 1.530(6) | C (5) -C (6) | 1.396(5) |
| C (5) -C (18) | 1.518(6) | C (6) -C (20) | 1.519(6) |
| C (7) -C (8) | 1.532(6) | C (8) -C (9) | 1.526(6) |
| C (9) -C (10) | 1.467(6) | C (10)-C (11) | 1.185(5) |
| C (11)-C (12) | 1.388(5) | C (12)-C (13) | 1.182(5) |
| C (13)-C (14) | 1.462(6) | C (14)-C (15) | 1.506(6) |
| C (15)-C (16) | 1.537(6) | | |
| C ( *i* )-H ( *i* ) | | | |
| Average | 0.98 | | |
| Range | 0.92—1.04 | | |
| (b) [3.4]Paracyclophadiyne | | | |
| C (1) -C (2) | 1.392(7) | C (1) -C (6) | 1.383(7) |
| C (1) -C (17) | 1.513(8) | C (2) -C (3) | 1.385(7) |
| C (3) -C (4) | 1.372(7) | C (4) -C (5) | 1.396(7) |
| C (4) -C (7) | 1.514(8) | C (5) -C (6) | 1.362(7) |
| C (7) -C (8a) | 1.418(13) | C (7) -C (8b) | 1.728(11) |
| C (8a)-C (9) | 1.375(12) | C (8b)-C (9) | 1.620(13) |
| C (9) -C (10) | 1.497(9) | C (10)-C (11) | 1.178(7) |
| C (11)-C (12) | 1.367(7) | C (12)-C (13) | 1.163(7) |
| C (13)-C (14) | 1.454(9) | C (14)-C (15) | 1.467(10) |
| C (15)-C (16) | 1.481(9) | C (16)-C (17) | 1.540(8) |
| C ( *i* )-H ( *i* ) | | | |
| Average | 1.00 | | |
| Range | 0.73—1.19 | | |

Table 8. Bond angles ($\phi$/°) and their standard deviations of nonhydrogen atoms

| | | | |
|---|---|---|---|
| (a) Tetramethyl[3.3]paracyclophadiyne | | | |
| C(2)-C(1)-C(6) | 119.4(3) | C(2)-C(1)-C(7) | 121.5(3) |
| C(6)-C(1)-C(7) | 119.2(3) | C(1)-C(2)-C(3) | 119.9(3) |
| C(1)-C(2)-C(19) | 120.4(3) | C(3)-C(2)-C(19) | 119.7(3) |
| C(2)-C(3)-C(4) | 120.5(4) | C(2)-C(3)-C(17) | 119.3(3) |
| C(4)-C(3)-C(17) | 120.2(4) | C(3)-C(4)-C(5) | 119.3(3) |
| C(3)-C(4)-C(16) | 121.3(4) | C(5)-C(4)-C(16) | 119.4(3) |
| C(4)-C(5)-C(6) | 120.0(3) | C(4)-C(5)-C(18) | 120.7(3) |
| C(6)-C(5)-C(18) | 119.4(3) | C(5)-C(6)-C(1) | 120.6(3) |
| C(5)-C(6)-C(20) | 118.8(3) | C(1)-C(6)-C(18) | 120.6(3) |
| C(1)-C(7)-C(8) | 114.6(3) | C(7)-C(8)-C(9) | 116.7(4) |
| C(8)-C(9)-C(10) | 112.8(4) | C(9)-C(10)-C(11) | 171.3(4) |
| C(10)-C(11)-C(12) | 169.8(4) | C(11)-C(12)-C(13) | 169.6(4) |
| C(12)-C(13)-C(14) | 173.6(4) | C(13)-C(14)-C(15) | 114.3(4) |
| C(14)-C(15)-C(16) | 117.9(4) | C(4)-C(16)-C(15) | 114.7(4) |
| (b) [3.4]Paracyclophadiyne | | | |
| C(2)-C(1)-C(6) | 117.6(4) | C(2)-C(1)-C(17) | 120.4(5) |
| C(6)-C(1)-C(17) | 122.0(4) | C(1)-C(2)-C(3) | 120.0(5) |
| C(2)-C(3)-C(4) | 122.5(5) | C(3)-C(4)-C(5) | 116.7(5) |
| C(3)-C(4)-C(7) | 121.5(5) | C(5)-C(4)-C(7) | 122.0(5) |
| C(4)-C(5)-C(6) | 121.5(5) | C(1)-C(6)-C(5) | 121.7(4) |
| C(4)-C(7)-C(8a) | 113.6(5) | C(4)-C(7)-C(8b) | 114.4(6) |
| C(7)-C(8a)-C(9) | 118.4(7) | C(7)-C(8b)-C(9) | 123.0(8) |
| C(8a)-C(9)-C(10) | 113.9(6) | C(8b)-C(9)-C(10) | 114.9(6) |
| C(9)-C(10)-C(11) | 173.2(6) | C(10)-C(11)-C(12) | 172.8(5) |
| C(11)-C(12)-C(13) | 176.4(5) | C(12)-C(13)-C(14) | 173.9(6) |
| C(13)-C(14)-C(15) | 109.2(6) | C(14)-C(15)-C(16) | 112.0(6) |
| C(15)-C(16)-C(17) | 110.5(5) | C(1)-C(17)-C(16) | 112.8(5) |

response to a number of methyl groups.18) In the molecule of (I), the distances of the atoms in the diacetylene group from the benzene plane are in the range from 3.019 to 3.256 Å, as is shown in Table 9, smaller than those of (III) by 0.01—0.04 Å. Some of the short intramolecular contacts are 3.203 of C(1)···C(10), 3.288 of C(2)···C(11), 3.259 of C(3)···C(12), and 3.153 Å of C(4)···C(13).

Since the methyl substituents on the benzene ring enhance the electron-donor property of the ring by reducing the $I_p$ of the ring (7.86 eV in hexamethylbenzene as compared to 9.24 eV of benzene), the EDA interaction is apparently stronger for this molecule than for unsubstituted [3.3]paracyclophadiyne. For instance, the peak of the first electronic-absorption band appears at 34200 cm$^{-1}$, while it is 35300 cm$^{-1}$ in the unsubstituted one, and the red shift of about 1100 cm$^{-1}$ means that the inter-ring interaction is enhanced. The CT transition from the benzene ring to the diacetylene group was found in (III) at 42700 cm$^{-1}$, while it is observed in this molecule at 40500 cm$^{-1}$. The lowering of the transition energy by 2200 cm$^{-1}$ is an indication of the stronger EDA interaction. The analysis of the MO involved in EDA interaction would seem to be of interest. As is shown in Fig. 8, the phase of the HOMO of hexamethylbenzene (which is degenerated) matches the LUMO of diacetylene. The HOMO-LUMO interaction which is necessary for the EDA complex is considerable for this system, while in other cyclophadiynes without methyl substituents, the EDA interaction is less favourable.

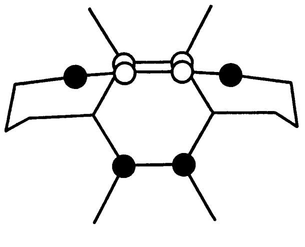

Fig. 8. Symmetries of MO. One of the HOMO of hexamethylbenzene and the LUMO of diacetylene groups are illustrated.

The mean value of the torsion angles around the methylene bridge is 70.5°, this indicates that the conformation are *gauche* as regards the internal rotation around the carbon-carbon bonds.

*Molecular Structure of* [3.4]*Paracyclophadiyne*. The

TABLE 9. DEVIATIONS ($l$/Å) FROM THE LEAST-SQUARES PLANE OF THE BENZENE RING

| Tetramethyl[3.3]paracyclophadiyne | | | | [3.4]Paracyclophadiyne | | | |
|---|---|---|---|---|---|---|---|
| Deviations | | Distances from the benzene plane | | Deviations | | Distances from the benzene plane | |
| C (1)[a)] | 0.035 | C (10) | 3.076 | C (1)[a)] | 0.002 | C (10) | 3.185 |
| C (2)[a)] | −0.022 | C (11) | 3.256 | C (2)[a)] | −0.001 | C (11) | 3.473 |
| C (3)[a)] | −0.012 | C (12) | 3.236 | C (3)[a)] | −0.003 | C (12) | 3.642 |
| C (4)[a)] | 0.033 | C (13) | 3.019 | C (4)[a)] | 0.005 | C (13) | 3.718 |
| C (5)[a)] | −0.020 | | | C (5)[a)] | −0.003 | | |
| C (6)[a)] | −0.014 | | | C (6)[a)] | 0.000 | | |
| C (7) | 0.187 | | | C (2) | −0.021 | | |
| C (16) | 0.163 | | | H (3) | −0.060 | | |
| C (17) | −0.006 | | | H (5) | −0.057 | | |
| C (18) | −0.110 | | | H (6) | −0.020 | | |
| C (19) | −0.063 | | | C (7) | 0.055 | | |
| C (20) | −0.051 | | | C (17) | 0.004 | | |

a) These atoms were included in the calculation of the least-squares plane.

average of the bond lengths of the benzene ring is 1.382 Å, which is shorter than the normal value (1.392—1.397 Å) and similar to that of (III). As in cyclophanes, it is observed that a benzene ring is distorted from a normal hexagon, with the endocyclic angle of C(1) and C(4) being 117.6 and 116.7° respectively, smaller than the rest by 4.3°. The carbon atoms of the benzene ring are almost coplanar, and no deviation of the hydrogen atoms toward the center of the molecule is found. The dihedral angles between the benzene plane and the planes through C(1), C(2), and C(6) and C(3), C(4), and C(5) are 0.6 and 0.2° respectively. The displacements of the carbon of para-substituted methylene are 0.004 Å for C(1) of the tetramethylene and 0.055 Å for C(17) of the trimethylene-bridge. These values are smaller than those of (III), and the benzene ring keeps a good planarity.

The bond lengths of the diacetylene group are the same as those of the other paracyclophadiynes. The bow-shape deformation, the mean bond angle of the carbon atoms of diacetylene, is 174.1°, smaller than in the case of (I) and (III) because of a less repulsive interaction due to a longer methylene-bridge and a larger spatial distances between the two groups. The larger bow-shape deformation compared to the benzene ring is due to the difference between the length and shapes in these two groups. The distances between the benzene ring and the C(10) and C(11) atoms of the moiety of the diacetylene group are 3.185 and 3.473 Å, and the shortest interatomic distance is 3.250 Å of C(4)···C(10). For the other moeity, the short intramolecular distances are 3.729 of C(1)···C(13), 3.747 of C(1)···C(12), and 3.769 Å of C(6)···C(12). As may be seen from the projection of the diacetylene group onto the benzene plane, the diacetylene group is nearly parallel to the direction of C(1)···C(4) of the benzene ring, the inclination being only 4°, similar to (III).

An unexpected feature of the structure is the disordered arrangement of the trimethylene-bridge. It is interesting that the disordered arrangement is found only on the trimethylene-bridge of the molecules of (II) and (III). The bond distances of this disordered methylene-bridge are 1.4—1.7 Å. The values of the bond lengths and angles, including those of the atoms of the disordered part, are less reliable. The average of the torsion angles of the two methylene-bridges is 67.2°, and it is apparent that the conformations are *gauche*, similar to those of other paracyclophadiynes.

The stereoscopic views of the crystal structure projected along the b-axis are shown in Fig. 7. All the intermolecular contacts are normal.

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