

Cerutti for his assistance in the preliminary stages of the analysis.

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The Crystal and Molecular Structure of [3,3]Paracyclophadiyne

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[3,3]Paracyclophadiyne crystallizes in the monoclinic system, space group $P2_1/a$, with lattice parameters $a = 14.509$ (2), $b = 8.539$ (1), $c = 10.623$ (1) Å and $\beta = 112.37$ (5)° at 10°C, and $Z = 4$. The atomic coordinates and anisotropic temperature factors have been refined by a full-matrix least-squares method to $R = 0.087$ based on 1691 structure factors measured on a Hilger–Watts diffractometer. The molecule consists of the benzene and diacetylene groups linked by two trimethylene bridges, one with a rigid conformation and the other with a disordered structure. The diacetylene chain is bent into a bow shape, and the distance between the two groups is about 3.1 Å, which is apparently shorter than normal interatomic distances between the aromatic ring atoms.

The transannular π -electron interactions have been extensively investigated for paracyclophanes by Cram and his coworkers and several interesting features have been reported on the properties of these highly symmetrical and crowded compounds (Cram & Cram, 1971). Evidence of an unusual feature in the aromatic ring has been shown by crystal structure analysis: a significant deformation of the benzene ring has been found in [2,2]paracyclophane (Brown, 1953*a*; Lonsdale, Milledge & Rao, 1960; Hope, Bernstein & Trueblood, 1972) and its tetrahydro- derivative (Coulter & Trueblood, 1963) and similar results have been observed for [2,2]metacyclophane (Brown, 1953*b*) and its derivative (Hanson, 1962) and [3,3]-paracyclophane (Gantzel & Trueblood, 1965), where the distortion of the aromatic ring has also been noticed.

Recently Misumi and coworkers have synthesized a series of paracyclophadiyne derivatives (Matsuoka, Negi, Otsubo, Sakata & Misumi, 1972) and the chemical and spectral properties have been investigated (Kaneda, Ogawa & Misumi, 1973; Takabe, Tanaka & Tanaka, 1974). Detailed analyses of the geometries of these molecules should be important in finding the transannular electron interaction between the benzene and diacetylene groups. In this paper a crystal structure analysis of [3,3]paracyclophadiyne is reported. The present molecule is not as symmetrical as the paracyclophanes; however, it will provide a novel interaction between the different groups through a transannular mode. The structure obtained shows the bent diacetylene group and a partial disorder in one of the trimethylene bridges.

Experimental

Crystals recrystallized from petroleum spirit were kindly provided by Drs Sakata, Kaneda and Misumi of Osaka University. The space group was determined from oscillation and Weissenberg photographs, and the density was measured by the flotation method. The cell dimensions were calculated by a least-squares treatment based on 12 sets of reflexion angles measured on a Hilger-Watts four-circle diffractometer.

Crystal data

$C_{16}H_{16}$ ($M=208.3$); monoclinic, space group $P2_1/a$; $a=14.509$ (2), $b=8.539$ (1), $c=10.623$ (1) Å, $\beta=112.37$ (5)°, Cu $K\alpha$ radiation, $\lambda=1.5418$ Å, at 10°C. Systematic absences: $h0l$ when h is odd, $0k0$ when k is odd, $Z=4$, $D_m=1.05$, $D_c=1.04$ g cm $^{-3}$.

All equivalent sets of independent reflexions, hkl , $h\bar{k}l$, $h\bar{k}\bar{l}$ and $h\bar{k}l$, within $\theta=78^\circ$, were measured by the $\omega-2\theta$ step scan method on a Hilger-Watts four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. The data were averaged to give a set of independent reflexions. The agreement between equivalent reflexions was estimated by a factor $\delta = \frac{\sum_h \sum_i |F_{hi}| - |\bar{F}_h|}{\sum_h \sum_i |F_{hi}|}$, where $|F_{hi}|$ is the structure amplitude of the i th equivalent, $|\bar{F}_h|$ the average value and h the Miller indices. The factor δ was found to be 0.04, which indicates a reasonable accuracy in the reflexion data.

The standard deviation for the averaged structure factor was estimated by $\sigma(\bar{F}) = \frac{1}{4} \left\{ \sum_{i=1}^4 \sigma^2(F_i) \right\}^{1/2}$ where $\sigma(F_i)$ was calculated from counting statistics. Any reflexion whose intensity did not exceed 3σ was regarded as unobserved. In all 1691 independent reflexions were obtained, and the unobserved amount to 845. The calculated structure amplitudes for unobserved reflexions were 1.0 on average. The linear absorption coefficient is 5.7 cm $^{-1}$, and no correction was made for absorption or extinction.

Structure determination and refinement

A sharpened three-dimensional Patterson synthesis was calculated and a reasonable structure was found after several trials. Least-squares refinement was carried out with isotropic temperature factors by the block-diagonal least-squares method. The temperature factors of all the carbon atoms except C(8) converged at 3–5 Å 2 , while that of C(8) remained 10 Å 2 . A Fourier map calculated without C(8) showed two peaks near both C(7) and C(9), one of which had an electron density of about two thirds that of the other carbon atoms and the other of about one third; this indicated disorder around C(8). All the hydrogen atoms except those around the disordered carbons were found in a difference map.

A full-matrix least-squares refinement was performed with different occupancies of the disordered

sites. In the refinement ten reflexions were omitted because they showed fairly large deviations. At this stage eight of twelve disordered hydrogen atoms, H(7b1), H(8b1), H(9b1) and H(9b2) being the four exceptions, could be found from the difference map (Fig. 1). Further calculations including these eight hydrogen atoms were carried out, and the positions of four of them did not converge. The positions of the eight missing hydrogen atoms were not refined, but the atoms were assumed to be attached to the disordered carbon atoms in a tetrahedral environment. The final calculation was carried out with anisotropic temperature factors for the carbon atoms, and with isotropic ones for all hydrogen atoms. The final R value was 0.078 for 1681 reflexions. The value was 0.087 when ten reflexions whose intensities may have suffered from extinction or other effects were included. All parameter shifts were less than one tenth of their estimated standard deviations.

Final atomic coordinates and anisotropic temperature factors of the carbon atoms are listed in Tables 1 and 2 respectively. The corresponding values for the hydrogen atoms including the assumed positions are

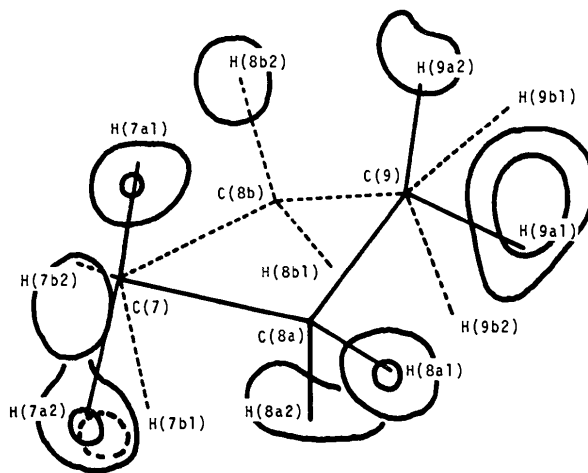


Fig. 1. Difference Fourier map around disordered atoms.

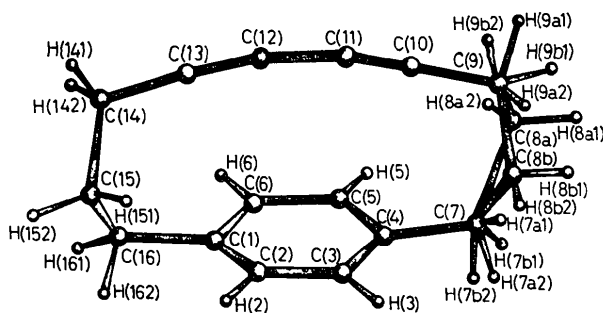


Fig. 2. Disordered molecular structure with conventional numbering of the atoms.

shown in Table 3. The structure is illustrated in Fig. 2 with the conventional numbering of the atoms.* The computations were carried out with the programs of the UNICS system and with own programs. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). All computations were performed by Facom 230-60 computers at Kyoto University and Nagoya University.

Results and discussion

The bond lengths and angles are listed in Tables 4 and 5 respectively. The bond lengths in the benzene ring are 1.374–1.387 Å, somewhat shorter than the values

* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31020 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic coordinates for carbon atoms with e.s.d.'s (in parentheses)*

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.1715 (2)	-0.0061 (4)	0.2397 (3)
C(2)	0.2350 (2)	0.0028 (4)	0.3750 (3)
C(3)	0.3087 (3)	0.1141 (4)	0.4212 (4)
C(4)	0.3220 (2)	0.2225 (4)	0.3327 (4)
C(5)	0.2564 (3)	0.2178 (4)	0.1979 (4)
C(6)	0.1825 (2)	0.1051 (4)	0.1522 (4)
C(7)	0.4078 (3)	0.3380 (5)	0.3816 (6)
C(8a)	0.5165 (6)	0.2554 (10)	0.4163 (10)
C(8b)	0.4745 (9)	0.3369 (14)	0.3262 (13)
C(9)	0.5391 (3)	0.1807 (6)	0.3221 (7)
C(10)	0.4829 (3)	0.0363 (5)	0.2730 (4)
C(11)	0.4304 (3)	-0.0738 (5)	0.2352 (4)
C(12)	0.3576 (3)	-0.1880 (4)	0.1952 (4)
C(13)	0.2871 (3)	-0.2710 (4)	0.1666 (4)
C(14)	0.1911 (3)	-0.3540 (5)	0.1292 (6)
C(15)	0.1014 (3)	-0.2407 (5)	0.0821 (4)
C(16)	0.0933 (3)	-0.1340 (5)	0.1897 (4)

found for a normal benzene ring (1.392–1.397 Å), and are close to those found for [2,2]- and [3,3]paracyclophanes. A deformation from the hexagonal shape of the benzene ring is observed: the bond angles C(2)–C(1)–C(6) and C(3)–C(4)–C(5), 117.4° and 117.6° respectively, are smaller than the rest by 3.8°.

The equation of the least-squares plane for the benzene ring referred to the orthogonal set of axes *a*, *b* and *c'* is 0.7638*x* – 0.6145*y* – 0.1973*z'* = 0.7127. C(1) and C(4) of the benzene ring deviate 0.015 Å from the plane toward the diacetylene group and the other atoms, C(2), C(3), C(5) and C(6), are displaced by 0.008 Å in the opposite direction. The dihedral angles

Table 3. *Coordinates and isotropic temperature factors for hydrogen atoms with e.s.d.'s (in parentheses)*

The atoms marked with an asterisk are for assumed positions and their temperature factors are assumed to be 5.0.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(2)	0.227 (2)	-0.065 (4)	0.437 (3)	3.2 (8)
H(3)	0.355 (2)	0.120 (4)	0.524 (3)	5.3 (8)
H(5)	0.264 (3)	0.288 (5)	0.129 (4)	4.4 (9)
H(6)	0.138 (2)	0.095 (4)	0.051 (3)	3.1 (8)
H(7a1)	0.396 (5)	0.419 (8)	0.298 (7)	5.6 (18)
H(7a2)	0.418 (4)	0.410 (8)	0.478 (6)	7.0 (16)
H(7b1)*	0.449	0.322	0.481	5.0
H(7b2)*	0.383	0.448	0.368	5.0
H(8a1)	0.567 (4)	0.328 (7)	0.454 (6)	2.8 (13)
H(8a2)	0.536 (4)	0.153 (8)	0.489 (6)	4.2 (15)
H(8b1)*	0.517	0.425	0.379	5.0
H(8b2)*	0.431	0.374	0.234	5.0
H(9a1)*	0.612	0.158	0.365	5.0
H(9a2)*	0.526	0.256	0.246	5.0
H(9b1)*	0.575	0.199	0.261	5.0
H(9b2)*	0.588	0.155	0.415	5.0
H(141)	0.188 (3)	-0.435 (5)	0.050 (4)	8.7 (11)
H(142)	0.186 (3)	-0.399 (5)	0.217 (4)	4.6 (11)
H(151)	0.100 (3)	-0.168 (5)	-0.009 (4)	5.6 (10)
H(152)	0.030 (3)	-0.310 (5)	0.043 (4)	6.3 (10)
H(161)	0.097 (3)	-0.196 (5)	0.273 (4)	5.4 (11)
H(162)	0.023 (3)	-0.076 (5)	0.145 (4)	6.1 (10)

Table 2. *Anisotropic thermal parameters for carbon atoms*

Anisotropic temperature factors are of the form: $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$. $10^4 \times \beta_{ij}$ are given.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	52 (2)	158 (5)	124 (4)	4 (2)	41 (2)	-4 (4)
C(2)	68 (2)	179 (6)	115 (4)	-3 (3)	47 (3)	6 (4)
C(3)	75 (2)	160 (5)	127 (4)	1 (3)	38 (3)	-20 (4)
C(4)	70 (2)	130 (5)	162 (5)	3 (3)	46 (3)	-19 (4)
C(5)	76 (2)	137 (5)	153 (5)	14 (3)	52 (3)	24 (4)
C(6)	62 (2)	165 (6)	124 (4)	14 (3)	34 (3)	14 (4)
C(7)	103 (3)	147 (6)	233 (7)	-31 (4)	50 (4)	-30 (6)
C(8a)	84 (6)	203 (16)	185 (14)	-59 (7)	50 (7)	-43 (12)
C(8b)	75 (8)	176 (20)	129 (16)	-22 (10)	56 (9)	-5 (14)
C(9)	64 (3)	235 (8)	314 (10)	-11 (4)	54 (4)	35 (8)
C(10)	64 (2)	194 (7)	211 (6)	22 (3)	55 (3)	29 (5)
C(11)	62 (2)	192 (6)	162 (5)	27 (3)	44 (3)	7 (5)
C(12)	74 (2)	170 (6)	147 (5)	32 (3)	36 (3)	-11 (4)
C(13)	84 (3)	163 (6)	163 (5)	17 (3)	37 (3)	-29 (4)
C(14)	103 (3)	154 (6)	206 (7)	-14 (4)	33 (4)	-11 (6)
C(15)	78 (3)	222 (7)	161 (6)	-33 (4)	29 (3)	-26 (5)
C(16)	65 (2)	227 (7)	150 (5)	-24 (3)	38 (3)	-1 (5)

Table 4. Some bond distances with *e.s.d.*'s (Å)

C(1)—C(2)	1.383 (4)	C(2)—H(2)	0.91 (4)
C(2)—C(3)	1.374 (5)	C(3)—H(3)	1.05 (3)
C(3)—C(4)	1.384 (5)	C(5)—H(5)	0.98 (4)
C(4)—C(5)	1.387 (5)	C(6)—H(6)	1.03 (3)
C(5)—C(6)	1.383 (5)	C(7)—H(7a1)	1.09 (7)
C(6)—C(1)	1.381 (5)	C(7)—H(7a2)	1.15 (7)
C(4)—C(7)	1.517 (5)	C(8a)—H(8a1)	0.93 (6)
C(1)—C(16)	1.518 (5)	C(8a)—H(8a2)	1.13 (6)
C(7)—C(8a)	1.636 (10)	C(14)—H(141)	1.08 (5)
C(7)—C(8b)	1.310 (17)	C(14)—H(142)	1.04 (5)
C(15)—C(16)	1.501 (7)	C(15)—H(151)	1.14 (4)
C(8a)—C(9)	1.329 (13)	C(15)—H(152)	1.12 (4)
C(8b)—C(9)	1.640 (14)	C(16)—H(161)	1.02 (5)
C(14)—C(15)	1.545 (6)	C(16)—H(162)	1.08 (4)
C(9)—C(10)	1.461 (6)		
C(13)—C(14)	1.476 (6)		
C(10)—C(11)	1.180 (5)		
C(12)—C(13)	1.186 (5)		
C(11)—C(12)	1.380 (5)		

Table 5. Some bond angles with *e.s.d.*'s in parentheses

C(2)—C(1)—C(6)	117.3 (3)°
C(2)—C(1)—C(16)	121.2 (3)
C(6)—C(1)—C(16)	121.4 (3)
C(1)—C(2)—C(3)	121.9 (3)
C(2)—C(3)—C(4)	120.7 (3)
C(3)—C(4)—C(5)	117.6 (3)
C(3)—C(4)—C(7)	120.7 (3)
C(5)—C(4)—C(7)	121.6 (4)
C(4)—C(5)—C(6)	121.2 (4)
C(1)—C(6)—C(5)	121.0 (3)
C(4)—C(7)—C(8a)	113.1 (4)
C(4)—C(7)—C(8b)	119.5 (6)
C(7)—C(8a)—C(9)	122.0 (6)
C(7)—C(8b)—C(9)	123.0 (9)
C(8a)—C(9)—C(10)	114.2 (6)
C(8b)—C(9)—C(10)	116.7 (5)
C(9)—C(10)—C(11)	173.9 (5)
C(10)—C(11)—C(12)	170.7 (5)
C(11)—C(12)—C(13)	170.4 (5)
C(12)—C(13)—C(14)	172.0 (4)
C(13)—C(14)—C(15)	112.2 (3)
C(14)—C(15)—C(16)	115.8 (3)
C(1)—C(16)—C(15)	116.0 (4)

between the benzene plane and the planes through C(1), C(2) and C(6), and C(3), C(4) and C(5) are 1.8°. This tendency is more marked in [3,3]- and [2,2]paracyclophanes, where the angles are 6.4 and 12.6°, respectively. In the present molecule the deviation from planarity is not as significant as in other paracyclophanes. Both C(16) and C(7), which are adjacent to the benzene ring, are displaced towards the diacetylene group at distances of 0.07 and 0.12 Å from the benzene plane, respectively.

The bond lengths of the diacetylene group are nearly the same as those of diacetylenedicarboxylic acid (Dunitz & Robertson, 1947). One of the remarkable features is the bending of the diacetylene chain into a bow shape. Both triple bonds, C(10)—C(11) and C(12)—C(13), are bent from the central C(11)—C(12) bond to the benzene ring by 9.3° and 9.6°, respectively. C(9)—C(10) and C(13)—C(14) make angles of 6.1° and 8.0° with C(10)—C(11) and C(12)—C(13), respectively. These

bendings are mainly due to the repulsion of the electron clouds between the diacetylene and benzene groups, and to the differences between the lengths in these two groups. The linear projection of the diacetylene group onto the benzene ring showed that the diacetylene chain is nearly parallel, but is actually inclined 2.5° to the diagonal of the benzene ring. In [2,2]paracyclophane both benzene rings are staggered in order to relieve the repulsive interactions between the eclipsed hydrogens.

The distances between the atoms of the diacetylene group and the plane of the benzene ring are in the range 3.05–3.26 Å (Table 6). These values are comparable to or even smaller than those of [3,3]-paracyclophane, which are 3.14–3.39 Å (Gantzel & Trueblood, 1965). This result is reasonable since the repulsion between the faced atoms may be reduced in the present system because the diacetylene group is linear and is not overlapped directly by the atoms of the benzene ring. The shorter interatomic distances between the atoms of the benzene ring and the diacetylene group are shown in Fig. 3. The shortest are 3.09 Å for C(4)···C(10) and C(1)···C(13), with 3.31 Å for C(1)···C(12) and 3.35 Å for C(4)···C(11). Recent chemical study (Kaneda, Ogawa & Misumi, 1973) showed that the addition of TCNE to this molecule occurs from the side of the diacetylene group accompanied by ring fusion between these shorter

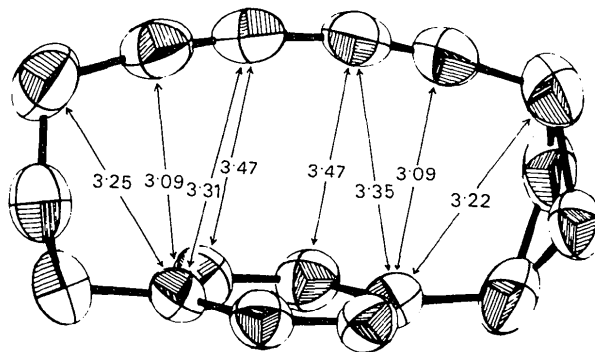


Fig. 3. Interatomic distances between the benzene and diacetylene groups.

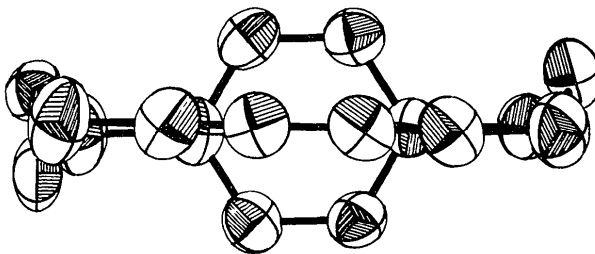


Fig. 4. Thermal ellipsoids viewed from the top of the molecule.

contact atoms at C(1)···C(13) and C(4)···C(11) or C(1)···C(12) and C(4)···C(10).

One more unexpected feature of the structure is the disordered arrangement of the trimethylene bridge. In spite of the disorder on one side, no disorder is found for the corresponding atom C(15) in the other bridge. Although the disorder of the bridge atom obeying the crystal symmetry is known (Hanson & Macauley, 1972), only one case has been reported on the trimethylene bridge (Frank & Paul, 1973). Moreover, different occupancies of the disordered atoms in

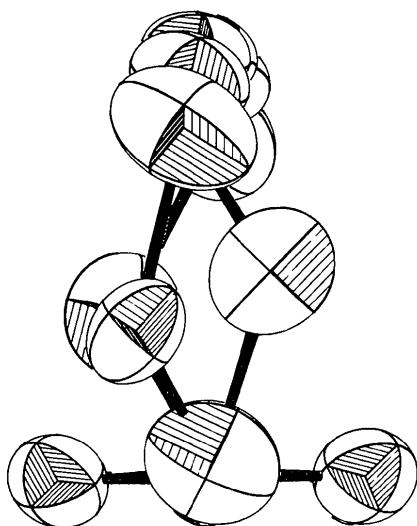


Fig. 5. Thermal ellipsoids viewed from the side of the molecule.

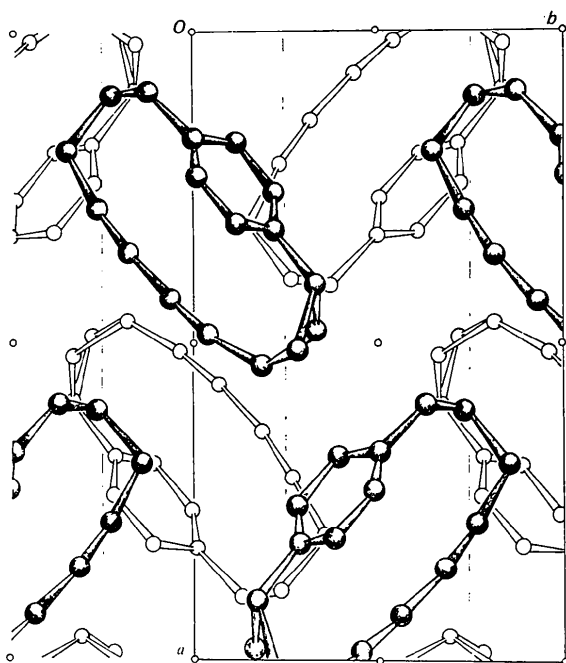


Fig. 6. Crystal structure projected along the *c* axis.

Table 6. Deviations from the least-squares plane of the benzene ring and distances between the diacetylene group and the benzene plane

Deviations		Distances from the benzene plane	
C(1)*	0.015 Å	C(10)	3.076 Å
C(2)*	-0.008	C(11)	3.262
C(3)*	-0.007	C(12)	3.256
C(4)*	0.015	C(13)	3.053
C(5)*	-0.009		
C(6)*	0.007		
C(7)	0.115		
C(16)	0.070		
H(2)	-0.050		
H(3)	-0.040		
H(5)	0.049		
H(6)	0.059		

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

the chain are known only for the sulphur atom (Davis & Bernal, 1971). In this molecule C(8*a*) is in a position related to C(15) by C_2 symmetry, while C(8*b*) is situated in the position of mirror symmetry with respect to C(15).

The observed bond distances around the disordered atoms differ from carbon-carbon single-bond values; namely the values for two different conformations are C(7)-C(8*a*)=1.64 Å and C(8*a*)-C(9)=1.33 Å, and C(7)-C(8*b*)=1.31 Å and C(8*b*)-C(9)=1.64 Å. The bond distance itself may not be accurate because of the disorder; the disordered C(8) atom was resolved into two different sites, but the neighbouring atoms, C(7) and C(9), were not separated and were found as single peaks. The thermal motion ellipsoids are illustrated in Figs. 4 and 5, and it is found that C(7) and C(9) show significant anisotropies, which may be due to the disorder of these atoms. The largest principal axes of the thermal motion ellipsoids are directed towards the shorter bond directions, and it may mean that the true atomic positions are actually disordered and not on apparent centres. Recently (Furusaki, Hamanaka & Matsumoto, 1973, 1974), the significant short bond distances observed with cyclohexene derivatives were explained by the disorder of the atomic positions.

Such an anomalous structure may be explained as follows; a hyperconjugation may possibly exist between the pseudo- π orbitals of the trimethylene bridge with the π orbitals of the diacetylene group and to a lesser extent with the pseudo- π orbitals composed of the $2p\sigma$ orbitals of the benzene ring, because the geometry of the trimethylene bridge is favourable for hyperconjugation. Two conformations of the trimethylene bridge mean that the hyperconjugation or other steric effects are important in distorting the normal chain structure but are not strong enough to give rise to an unusually stable single conformation. Another reason for the disorder may be that the tri-

methylene bridge is inserted between the two different conjugated systems. A recent structural analysis on *N*-acetyl-L-prolyl-L-lactylmethylamide (Lecomte, Aubry, Protas, Boussard & Marraud, 1974) shows that a similar disorder occurs around the prolyl group.

The torsional angle around the trimethylene bridge at C(13)–C(14)–C(15)–C(16) is -67.3° , while those for the disordered bridge are -67.7° [C(10)–C(9)–C(8a)–C(7)] and 49.6° [C(10)–C(9)–C(8b)–C(7)]. The torsional angle of C(4)–C(7)–C(8a)–C(9) is 61.5° and that of C(4)–C(7)–C(8b)–C(9) is -56.5° . All these conformations showed *gauche* forms as regards the internal rotation around the carbon–carbon bonds.

The packing of the molecules projected along the *c* axis is shown in Fig. 6 and the intermolecular contacts

Table 7. Intermolecular distances less than 3.7 Å between non-hydrogen atoms

Code for symmetry-related atoms	
Superscript	Atom at
None	<i>x</i> , <i>y</i> , <i>z</i>
(i)	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, <i>z</i>
(ii)	$\frac{1}{2}-x$, $\frac{1}{2}+y$, $-z$
(iii)	$\frac{1}{2}+x$, $-\frac{1}{2}-y$, <i>z</i>
C(11)···C(16 ⁱⁱⁱ)	3.59 Å
C(1)···C(8b ⁱ)	3.62
C(16)···C(8b ⁱ)	3.66
C(1)···C(9 ⁱ)	3.67
C(5)···C(13 ⁱⁱ)	3.68

less than 3.7 Å are listed in Table 7. The packing around C(8) is rather loose so that the disordered structure may be allowed. No particularly short intermolecular distances were found in this structure, and the shortest is 3.59 Å for C(11)···C(16).

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