

Tableau 2. Distances interatomiques avec leurs écarts-type entre parenthèses compte tenu des incertitudes sur les paramètres de la maille (en Å)

Sn—S(2)	2,376 (3)	Eu(2)—S(3)	2,989 (2) × 2
Sn—S(3)	2,448 (4)	Eu(2)—S(4)	3,019 (1) × 2
Sn—S(1)	2,467 (2)	Eu(2)—S(2)	3,071 (3) × 2
Sn—S(1)	2,467 (2)	Eu(2)—S(1)	3,148 (3)
Sn—S(4)	2,971 (2)	Eu(2)—S(1)	3,303 (3)
Eu(1)—S(3)	3,159 (3) × 4		
Eu(1)—S(2)	3,196 (3) × 4		

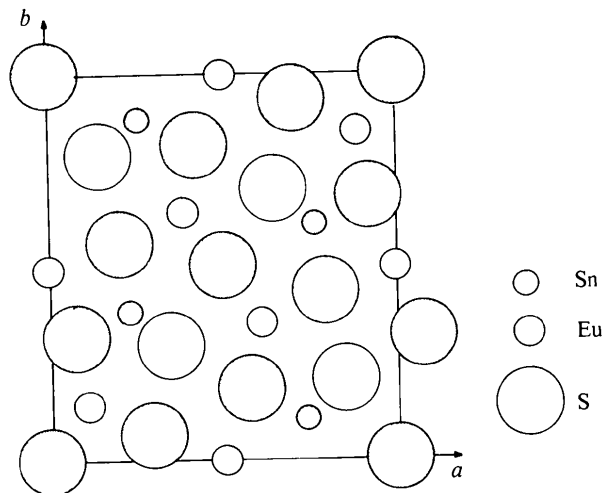


Fig. 1. Projection de la maille parallèlement à la direction  $c$ . Les atomes de cote  $z = 0$  sont laissés en blanc, ceux de la cote  $z = \frac{1}{2}$  sont en gris.

déplacé vers l'une des faces de ce tétraèdre et se trouve alors en présence du cinquième atome de soufre avec lequel il échange une liaison plus longue. Cette coordination peu courante de l'étain a déjà été rencontrée lors de l'étude de  $\text{Eu}_3\text{Sn}_3\text{S}_{12}$  (Jaulmes & Julien-Pouzol, 1977). Mais alors que dans ce dernier composé

les cinq liaisons Sn—S avaient des longueurs voisines et semblables aux quatre liaisons courtes de  $\text{Eu}_3\text{Sn}_2\text{S}_7$  (2,44 Å en moyenne), ici la cinquième est nettement plus longue.

Les atomes d'euporium ont des coordinences égales à 8. Le premier Eu(1) est à l'intérieur d'un prisme dont les bases forment un quadrilatère peu différent d'un carré. Le deuxième Eu(2) est à l'intérieur d'un prisme à bases triangulaires constituées par trois atomes de soufre ( $z = \frac{1}{2}$ ) et leurs trois homologues ( $z = -\frac{1}{2}$ ). Dans le plan équatorial des prismes contenant cet europorium se trouvent deux atomes de soufre qui forment avec lui des liaisons approximativement normales aux faces latérales du prisme. Ces liaisons sont plus longues que les six autres. Les deux atomes d'euporium, bien qu'ayant des environnements différents, possèdent la même coordinence. La valeur moyenne des distances Eu—S pour chacun de ces deux atomes d'euporium est respectivement égale à 3,17 et 3,075 Å. Ces deux valeurs peuvent être qualifiées de normales pour des europorium(II). Elles sont très voisines de celles qui ont été trouvées lors de l'étude de la structure cristalline de  $\text{Eu}_3\text{Sn}_3\text{S}_{12}$  (Jaulmes & Julien-Pouzol, 1977): 3,06 Å en moyenne.

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## Bis(*m*-chlorophenyl)acetylene

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**Abstract.**  $\text{C}_{14}\text{H}_8\text{Cl}_2$ , monoclinic,  $C2/c$ ,  $a = 27.201$  (7),  $b = 5.758$  (1),  $c = 7.647$  (2) Å,  $\beta = 102.11$  (5)°,  $V =$

$1171.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.401$ ,  $D_m = 1.39$  g cm<sup>-3</sup> (flotation in  $\text{AgNO}_3$  solution at 25°C). The crystal structure was determined by the heavy-atom method and full-matrix least-squares refinement led to  $R =$

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0.057,  $R_w = 0.062$  for the 941 observed reflections. The molecules are centrosymmetric and therefore have zero dipole moment, but there are small deviations from planarity.

**Introduction.** Liberles & Matlosz (1971) pointed out that three possible orientations of the two aromatic rings in diarylalkynes may exist: a coplanar geometry arising from the overlap of the  $p$  orbitals of both aromatic rings with the same set of  $p$  orbitals of the alkyne; a perpendicular geometry which occurs when the  $\pi$  system of one aromatic ring overlaps one set of  $p$  orbitals of the alkyne, while that of the second ring overlaps the other; and the occurrence of a freely rotating system due to the cylindrical symmetry of the alkyne. The third possibility can only exist if the coplanar and perpendicular geometries have the same energies, to allow internal rotation.

Their quantum mechanical calculations, using the CNDO and INDO\* methods, predicted that the diarylalkynes should exist in the perpendicular form. The magnitude of the difference in energy between the coplanar and perpendicular geometries, however, was very small, only 1 kcal mol<sup>-1</sup>, and consequently the system should have a relatively unhindered rotation.

In the solid state diphenylacetylene was known to be essentially planar from X-ray analysis (Robertson & Woodward, 1937; Espiritu & White, 1977), and the ultraviolet absorption spectrum seemed to indicate that it was also planar in solution in contradiction to the calculated prediction. However, the dipole moment of bis(*m*-chlorophenyl)acetylene was measured as  $1.7 \pm 0.1$  D. The dipole moment for the *cis*-planar form would be 2.7 D, that for the perpendicular geometry, and also for a freely rotating molecule, 1.9 D. For the *trans*-planar form the dipole moment would be zero. Thus, it appeared that in solution, at least, different forms of the molecule co-existed. Only one type of crystal was obtained from the solution and an X-ray

\* Complete Neglect of Differential Overlap and Intermediate Neglect of Differential Overlap, approximate methods for obtaining molecular orbitals for all valence electrons.

study was undertaken to determine the molecular geometry in the solid state.

The X-ray data were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Cu  $K\alpha$  radiation using a crystal measuring  $0.12 \times 0.20 \times 0.15$  mm. The unit-cell parameters were obtained by a least-squares fit of angular data from 15 high-order reflections. The intensities were measured by the  $\omega$ - $2\theta$  scan method and the net intensities corrected for Lorentz–polarization effects including polarization by the monochromator. Absorption corrections were not made and from the shape of the crystal it is calculated [ $\mu(\text{Cu } K\alpha) = 47.02 \text{ cm}^{-1}$ ] that maximum absorption errors amount to  $\pm 9\%$  in  $F$ . Of 1179 reflections with  $\theta < 75^\circ$ , 941 were accepted as observed on the criterion  $I/\sigma_i \geq 2$ .

The structure was solved by the heavy-atom method, the H atoms being derived from a difference map after refinement of the Cl and C parameters. The molecular centers coincide with symmetry centers. Refinement was carried out by full-matrix least-squares methods minimizing  $\Sigma w(|F_o| - k|F_c|)^2$ . In the final stages  $w$  was included as  $1/|\Delta F|^2$  where  $|\Delta F|$  was obtained from a smoothed plot of  $|\Delta F|$  vs  $F_o$  and was  $0.53 + 1.3 \times 10^{-2}F_o + 1.2 \times 10^{-4}F_o^2$  for  $F_o \geq 5$  and  $0.74 - 3.1 \times 10^{-2}F_o + 1.5 \times 10^{-3}F_o^2$  for  $F_o < 5$ . Refinement of the H positions gave somewhat unreasonable irregularities and they were therefore maintained in regularized positions at the average C–H distance of 1.04 Å. The final refinement cycle gave  $R = 0.057$ ,  $R_w = 0.062$  and  $[\Sigma w(\Delta F)^2/(m - n)]^{1/2} = 0.79$  for all observed reflections. Including the unobserved reflections  $R$  was 0.067. The mean and maximum shift/e.s.d. were 0.02 and 0.10. The final difference electron density map showed residual density of  $\pm 0.26 \text{ e } \text{Å}^{-3}$ . The atomic coordinates are given in Table 1.\* The scattering

\* Tables of thermal parameters and of calculated and observed structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32878 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional atomic coordinates

	x	y	z
Cl	0.21149 (3)	-0.0230 (2)	0.1530 (1)
C(1)	0.0671 (1)	0.1502 (7)	-0.0012 (4)
C(2)	0.1114 (1)	0.0347 (6)	0.0726 (4)
C(3)	0.1570 (1)	0.1312 (7)	0.0655 (4)
C(4)	0.1605 (1)	0.3473 (7)	-0.0121 (5)
C(5)	0.1167 (1)	0.4625 (7)	-0.0837 (5)
C(6)	0.0703 (1)	0.3705 (7)	-0.0800 (5)
C(7)	0.0197 (1)	0.0466 (7)	-0.0002 (5)
H(1)	0.109	-0.127	0.128
H(2)	0.195	0.419	-0.018
H(3)	0.119	0.624	-0.138
H(4)	0.038	0.459	-0.134

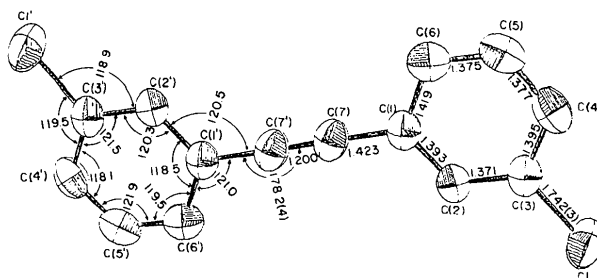


Fig. 1. Bond distances and bond angles in bis(*m*-chlorophenyl)acetylene. The standard deviations in the C–C bond lengths are 0.004–0.006 Å, and, in the bond angles, those that are not shown are 0.3°. The bond distances have been corrected for librational motion. The vibration ellipsoids are drawn at 50% probability.

factors used are those given in *International Tables for X-ray Crystallography* (1962). All computations were carried out with NRC programs (Ahmed, Hall, Pippy & Huber, 1973) and *ORFLS* (Busing, Martin & Levy, 1962).

**Discussion.** The finding of ordered, centrosymmetric molecules in the crystal structure does not help explain the dipole moment observed in solution. It appears that the gain in van der Waals energy in packing essentially planar molecules is greater than the loss by not adopting the favored configuration, or equilibrium between different configurations, in solution. This is not surprising in view of the small magnitude of the rotational barrier, and the situation is reminiscent of the case of biphenyl which is planar in the crystal (Hargreaves, Rizvi & Trotter, 1961) but not in the gas phase (Karle & Brockway, 1944).

The bond distances and angles are shown in Fig. 1. The distances have been corrected for librational motion (Schomaker & Trueblood, 1968). These corrections are small ( $\leq 0.006$  Å) and the corresponding

angular corrections, which are negligible, have not been applied. The bonds in the benzene ring average 1.388 (2) Å. The formal single bond C(1)–C(7) between the benzene ring and the triple bond is severely shortened. The molecule is not exactly planar, as shown in Table 2. Plane 1 is the least-squares mean plane of the asymmetric unit and this is displaced from the molecular center (origin) by 0.048 Å. Plane 2 is the least-squares mean plane of the whole molecule. The deviations from the plane are small on an absolute basis but seem large for packing-induced distortions. However, no intramolecular interactions can be found which would account for them. All van der Waals distances appear normal.

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Table 2. *Least-squares planes and atomic displacements from the planes*

Plane 1 is defined by the asymmetric unit only, plane 2 by the whole molecule.

$$\begin{aligned} \text{Plane 1} & 0.168X - 0.433Y - 0.886Z = -0.048 \\ \text{Plane 2} & 0.179X - 0.425Y - 0.887Z = 0 \end{aligned}$$

	$d_1$ (Å)	$d_2$ (Å)
Cl	0.020	0.026
C(1)	-0.011	-0.033
C(2)	-0.029	-0.045
C(3)	-0.011	-0.010
C(4)	0.001	0.015
C(5)	0.007	0.016
C(6)	-0.002	-0.010
C(7)	0.023	-0.017

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