Crystal Structure of the Doubly Bridged Biphenyl, 2-Chloro-4,5,9,10-Tetrahydropyrene

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The title compound (I) crystallizes in space group $P2_1/c$ with a = 8·509 ± 0·001, b = 8·094 ± 0·002, c = 26·031 ± 0·003 Å, β = 92·38 ± 0·09° and Z = 6. The structure was solved from *X*-ray diffraction data by Patterson and Fourier methods and refined by block-diagonal least-squares techniques to R 0·086 for 1252 observed reflections measured on a diffractometer. The analysis shows two crystallographically distinct molecules of different conformation, one of which is disordered. These configurations are associated with different orientations of the ethylene bridges. In one molecule the angle between the planes of the two benzene rings is 16·9°, whereas in the other it is close to zero.

THE presence of optical activity in substituted biphenyls has been ascribed to hindered rotation about the 1,1′-carbon–carbon bond arising from the repulsion of substituents in the *ortho*-position.[1-3] Repulsion is at a minimum when the planes of the rings are mutually perpendicular. Opposing such a rotation is a resonance effect involving electronic interactions between the two rings, maximum stabilisation occurring when the two rings are coplanar. In the absence of restraints, such as crystal packing forces, any given molecule will be expected to assume the configuration of minimum potential energy for the sum of these two opposing effects.[4]

The molecule 9,10-dihydrophenanthrene can take up a strainless conformation with an angle between the rings of *ca.* 16°. The introduction of a second ethylene bridge, as in 4,5,9,10-tetrahydropyrene, however, cannot be made without the production of some torsional strain, and it is not clear which conformation would be thermodynamically preferred. Among the possibilities which need to be considered are arrangements with the two benzenoid rings coplanar, parallel, or collinear with an angle between them of *ca.* 16°. Models suggest that all three possibilities would be rather similar in energy.

The results of u.v. spectral[5-7] and kinetic studies[5,8] on 4,5,9,10-tetrahydropyrene and related molecules

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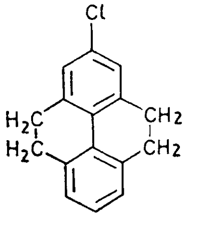
indicate that the torsional angle varies with the nature of the bridging atoms but that it is probably close to zero for the parent compound.

To assess this deduction and to provide a basis for further studies a single-crystal *X*-ray analysis of the


(I)

chloro-derivative, 2-chloro-4,5,9,10-tetrahydropyrene (I), was undertaken.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{13}Cl$, $M = 240{\cdot}7$. Monoclinic, $a = 8{\cdot}509 \pm 0{\cdot}001$, $b = 8{\cdot}094 \pm 0{\cdot}002$, $c = 26{\cdot}031 \pm 0{\cdot}003$ Å, $\beta = 92{\cdot}38 \pm 0{\cdot}09°$, $U = 1791$ Å^3, $D_m = 1{\cdot}30$, $Z = 6$, $D_c = 1{\cdot}34$, $F(000) = 756$. Space group $P2_1/c$, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 25·8 cm^{-1}.

Data were collected on a Hilger and Watts automatic diffractometer by use of a 2θ—ω scan. A total of 1252 independent reflections were recorded for which $I > 3\sigma$ (I). Absorption corrections were applied according to the method of Busing and Levy.[9]

The presence of one and a half molecules in the asymmetric unit suggests that the half molecule lies at a centre of inversion, disorder then being implied since the molecule cannot possess such symmetry. Atomic sites for the molecules lying in the general positions of the space group (the ' general ' molecule) were determined from a three-dimensional Patterson function and subsequent electron-density maps. After initial refinement of this molecule by the block-diagonal least-squares procedure a difference-Fourier synthesis revealed two half-weighted disordered molecules lying across the centre of symmetry such that the carbon atoms of both orientations approximately coincided.

Block-diagonal least-squares refinement on chlorine and carbon atoms was then continued, atoms in the ' disordered molecule ' being appropriately weighted. Hydrogen atoms were excluded, the other atoms being initially assumed to have isotropic thermal motion. Later an anisotropic model was allowed and refinement converged at *R* 0·122. Atoms of the ' disordered ' molecules showed some elongation of peaks on the electron-density map, no doubt reflecting non-coincidence of the two orientations. Elongation of the peak ascribed to C(21) was particularly marked and the bond distance C(20)–C(21) was shorter than expected. It was thus clear that the anisotropic model for this atom was inadequate to describe the physical situation. To improve the model C(21) was replaced by two half-weighted atoms lying along the major axis of the ellipsoid of vibration and when these were included with isotropic thermal constraints applied to them *R* was reduced slightly to 0·119. Hydrogen atom positions, except those associated with C(20) and C(21), were calculated (C–H assumed as 1·0 Å), confirmed from a difference-Fourier synthesis, and incorporated into a structure-factor calculation with isotropic thermal motion (*B* 5·0 Å^2) assumed. The *R* factor was reduced to 0·102. Further least-squares refinement with hydrogen atoms held in their calculated positions resulted in a final *R* of 0·086. Atomic scattering factors for chlorine, carbon, and hydrogen were taken from those listed in ref. 10. The weights applied to individual reflections in the refinement were based on the counting statistics and were of the form: $w = 4F_o^2/[\sigma(F_o^2) + 0{\cdot}6F_o^2]^2$.

RESULTS AND DISCUSSION

Final atomic co-ordinates and thermal parameters together with their standard deviations are listed in Tables 1 and 2. The numbering system is shown in Figure 1, bond lengths and angles with their standard deviations are given in Tables 3 and 4.† The mean standard deviations in bond lengths and angles are

TABLE 1

Fractional atomic co-ordinates and isotropic thermal parameters with standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
Cl(1)	0·2203(2)	0·2674(3)	0·09400(7)	
Cl(2)	0·9436(8)	0·3881(9)	0·4727(3)	
C(1)	0·3516(8)	0·2191(8)	0·1884(3)	
C(2)	0·3783(8)	0·2211(9)	0·1367(3)	
C(3)	0·5234(9)	0·1166(9)	0·1166(3)	
C(4)	0·8103(8)	0·1182(9)	0·1316(3)	
C(5)	0·8966(9)	−0·0107(10)	0·1647(3)	
C(6)	1·0198(8)	−0·0032(9)	0·2553(3)	
C(7)	1·0100(9)	0·0352(9)	0·3068(3)	
C(8)	0·8745(9)	0·1064(9)	0·3253(3)	
C(9)	0·6034(9)	0·2242(9)	0·3103(3)	
C(10)	0·4558(8)	0·1626(8)	0·2797(3)	
C(11)	0·4742(7)	0·1758(8)	0·2227(2)	
C(12)	0·6245(7)	0·1438(8)	0·2031(2)	
C(13)	0·6455(7)	0·1509(8)	0·1508(2)	
C(14)	0·8940(8)	0·0320(8)	0·2205(3)	
C(15)	0·7598(7)	0·1040(8)	0·2399(2)	
C(16)	0·7492(8)	0·1407(8)	0·2911(3)	
C(17)	0·828(1)	0·137(2)	0·5125(4)	
C(18)	0·809(1)	0·267(1)	0·4815(4)	
C(19)	0·665(1)	0·295(2)	0·4568(4)	
C(20)	0·383(1)	0·222(2)	0·4367(5)	
C(21a)	0·241(2)	0·126(2)	0·4533(7)	7·1(4)
C(21b)	0·314(2)	0·104(2)	0·4285(6)	6·0(3)
C(22)	0·711(1)	0·030(1)	0·5211(3)	
C(23)	0·564(1)	0·058(1)	0·4957(3)	
C(24)	0·540(1)	0·192(1)	0·4627(3)	
H(1)	0·24(1)	0·25(1)	0·203(4) *	
H(3)	0·54(1)	0·19(1)	0·076(4)	
H(4a)	0·88(1)	0·23(1)	0·131(4)	
H(4b)	0·80(1)	0·08(1)	0·092(4)	
H(5a)	1·02(1)	−0·02(1)	0·153(4)	
H(5b)	0·84(1)	−0·13(1)	0·158(4)	
H(6)	1·13(1)	−0·06(1)	0·242(4)	
H(7)	1·11(1)	0·01(1)	0·334(4)	
H(8)	0·87(1)	0·14(1)	0·366(4)	
H(9a)	0·61(1)	0·36(1)	0·307(4)	
H(9b)	0·59(1)	0·20(1)	0·351(4)	
H(10a)	0·35(1)	0·23(1)	0·289(4)	
H(10b)	0·43(1)	0·04(1)	0·289(4)	
H(17)	0·94(1)	0·12(1)	0·532(4)	
H(19)	0·65(1)	0·40(1)	0·431(4)	

* *B* = 5·0 Å^2 for all H atoms.

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† Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20591 (2 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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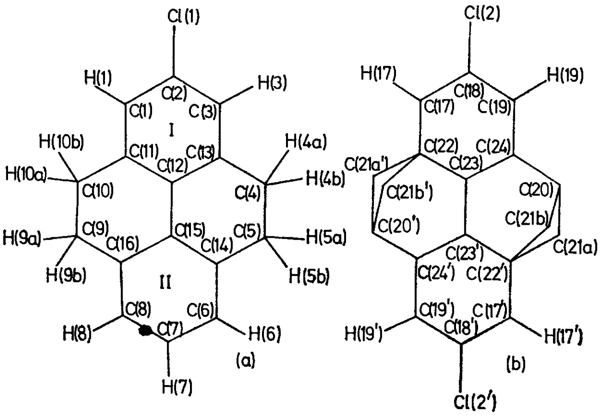

FIGURE 1 The crystallographic numbering system for (a) the ' general ' and (b) the ' disordered ' molecule

TABLE 2

Anisotropic thermal parameters * [$\times 10^4$ for Cl(1), $\times 10^3$ for all other atoms], with standard deviations in parentheses

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cl(1)	202(3)	363(5)	240(3)	132(7)	–33(2)	10(2)
Cl(2)	42(1)	46(1)	42(1)	–36(2)	0(7)	1(8)
C(1)	14(1)	14(1)	21(1)	3(2)	–8(6)	–12(6)
C(2)	14(1)	19(1)	19(1)	5(2)	–31(5)	8(7)
C(3)	17(1)	18(1)	20(1)	1(2)	–6(6)	10(7)
C(4)	17(1)	19(1)	20(1)	–1(2)	32(6)	–6(7)
C(5)	16(1)	19(1)	23(1)	5(2)	22(6)	–11(7)
C(6)	13(1)	17(1)	32(1)	1(2)	–9(7)	5(9)
C(7)	20(1)	16(1)	27(1)	–3(2)	–26(7)	9(8)
C(8)	24(1)	17(1)	22(1)	–1(2)	–10(7)	2(7)
C(9)	20(1)	16(1)	19(1)	–2(2)	4(6)	–17(7)
C(10)	17(1)	15(1)	19(1)	2(2)	17(6)	–1(7)
C(11)	14(1)	11(1)	18(1)	–3(2)	5(6)	–1(6)
C(12)	14(1)	13(1)	17(1)	–1(2)	–11(5)	–5(6)
C(13)	14(1)	12(1)	19(1)	–3(2)	8(6)	–9(6)
C(14)	14(1)	13(1)	24(1)	–1(2)	6(6)	22(7)
C(15)	15(1)	12(1)	17(1)	–2(2)	1(6)	8(6)
C(16)	16(1)	11(1)	19(1)	–3(2)	–11(6)	18(6)
C(17)	44(2)	40(3)	28(2)	8(5)	–94(11)	–17(12)
C(18)	33(2)	42(2)	30(2)	–17(4)	–14(10)	–75(11)
C(19)	42(2)	42(3)	24(2)	22(4)	21(11)	11(13)
C(20)	24(2)	69(4)	55(3)	16(5)	–55(12)	193(15)
C(22)	36(2)	28(2)	24(1)	5(3)	–70(9)	–39(9)
C(23)	31(2)	32(2)	11(1)	29(2)	–19(7)	–15(7)
C(24)	30(2)	43(2)	18(1)	20(4)	22(8)	28(10)

* The scattering factor of an atom is expressed by:

$$f = f_0 \exp\{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}.$$

TABLE 3

Bond lengths (Å), with standard deviations in parentheses

(*a*) ' General ' molecule

Cl(1)–C(2)	1·750(7)	C(7)–C(8)	1·39(1)
C(1)–C(2)	1·37(1)	C(8)–C(16)	1·39(1)
C(1)–C(11)	1·39(1)	C(9)–C(10)	1·54(1)
C(2)–C(3)	1·38(1)	C(9)–C(16)	1·52(1)
C(3)–C(13)	1·38(1)	C(10)–C(11)	1·50(1)
C(4)–C(13)	1·53(1)	C(11)–C(12)	1·42(1)
C(4)–C(5)	1·52(1)	C(12)–C(13)	1·38(1)
C(5)–C(14)	1·49(1)	C(12)–C(15)	1·50(1)
C(6)–C(14)	1·40(1)	C(14)–C(15)	1·40(1)
C(6)–C(7)	1·38(1)	C(15)–C(16)	1·37(1)

(*b*) ' Disordered ' molecule

Cl(2)–C(18)	1·54(1)	C(20)–C(21b)	1·14(3)
C(17)–C(18)	1·33(2)	C(21a)–C(22′)	1·48(2)
C(17)–C(22)	1·34(2)	C(21b)–C(22′)	1·72(2)
C(18)–C(19)	1·37(2)	C(22)–C(23)	1·41(2)
C(19)–C(24)	1·37(2)	C(23)–C(23′)	1·46(2)
C(20)–C(24)	1·49(2)	C(23)–C(24)	1·39(2)
C(20)–C(21a)	1·52(3)		

TABLE 4

Bond angles (deg.), with standard deviations in parentheses

(*a*) ' General ' molecule

Cl(1)–C(2)–C(1)	118·1(7)	C(6)–C(14)–C(15)	117·7(8)
Cl(1)–C(2)–C(3)	118·2(7)	C(7)–C(6)–C(14)	120·4(8)
C(1)–C(2)–C(3)	123·7(8)	C(7)–C(8)–C(16)	119·1(8)
C(1)–C(11)–C(10)	123·1(8)	C(8)–C(16)–C(9)	119·6(8)
C(1)–C(11)–C(12)	118·6(8)	C(8)–C(16)–C(15)	120·0(8)
C(2)–C(1)–C(11)	118·8(8)	C(9)–C(16)–C(15)	120·3(8)
C(2)–C(3)–C(13)	117·3(8)	C(9)–C(10)–C(11)	111·7(8)
C(3)–C(13)–C(4)	120·4(8)	C(10)–C(9)–C(16)	110·3(8)
C(3)–C(13)–C(12)	121·4(8)	C(10)–C(11)–C(12)	118·4(8)
C(4)–C(5)–C(14)	111·4(8)	C(11)–C(12)–C(13)	120·1(8)
C(4)–C(13)–C(12)	118·1(8)	C(11)–C(12)–C(15)	119·2(8)
C(5)–C(4)–C(13)	111·2(8)	C(13)–C(12)–C(15)	120·8(8)
C(5)–C(14)–C(6)	122·6(8)	C(12)–C(15)–C(14)	118·3(8)
C(5)–C(4)–C(15)	119·5(8)	C(12)–C(15)–C(16)	119·5(8)
C(6)–C(7)–C(8)	120·8(8)	C(14)–C(15)–C(16)	122·0(8)

(*b*) ' Disordered ' molecule

Cl(2)–C(18)–C(17)	121(1)	C(20)–C(21a)–C(22′)	110(2)
Cl(2)–C(18)–C(19)	119(1)	C(20)–C(21b)–C(22′)	118(2)
C(17)–C(18)–C(19)	120(1)	C(20)–C(24)–C(28)	121(1)
C(17)–C(22)–C(21′a)	124(1)	C(21a)–C(20)–C(24)	120(1)
C(17)–C(22)–C(21′b)	108(1)	C(21a)–C(22′)–C(23′)	124(1)
C(17)–C(22)–C(23)	118(1)	C(21b)–C(20)–C(24)	113(2)
C(18)–C(17)–C(22)	122(1)	C(21b)–C(22′)–C(23′)	108(1)
C(18)–C(19)–C(24)	122(1)	C(22)–C(23)–C(23′)	119(1)
C(19)–C(24)–C(20)	122(1)	C(22)–C(23)–C(24)	121(1)
C(19)–C(24)–C(23)	117(1)	C(23)–C(23′)–C(24′)	120(1)

0·01 Å and 0·8° respectively for the ' general ' molecule, 0·02 Å and 1·0° for the ' disordered ' molecule. The higher values for the latter presumably arise from the non-coincidence of the disordered orientations. This is also suggested by the higher values of the root-mean-square amplitudes of thermal vibration (Table 5). The greatest effect is seen in the two carbon-atom chains which bridge the biphenyl where, as described earlier, C(21) was refined as two separate half-weighted carbons. Two such half-weighted atoms were not distinguished for C(20) but the root-mean-square amplitude of vibration along the major axis of the ellipsoid was the

TABLE 5

Root-mean-square amplitudes of vibration (Å $\times 10^3$)

Atom	Minor axis	Medium axis	Major axis
Cl(1)	223	312	361
Cl(2)	301	381	465
C(1)	203	223	276
C(2)	185	256	282
C(3)	231	248	271
C(4)	223	250	285
C(5)	218	263	286
C(6)	211	238	330
C(7)	227	252	324
C(8)	234	267	304
C(9)	218	264	273
C(10)	221	239	266
C(11)	190	232	251
C(12)	204	217	254
C(13)	195	229	255
C(14)	199	228	290
C(15)	196	230	246
C(16)	181	229	271
C(17)	256	357	450
C(18)	253	357	413
C(19)	283	326	430
C(20)	225	377	560
C(22)	233	304	405
C(23)	190	243	403
C(24)	242	297	407

highest observed (0·56 Å). These effects emphasise the limitations of the model suggested for the ' disordered ' molecule which must be regarded only as an approximation. Attempts were made to find more satisfactory positions for the bridge atoms from difference-Fourier maps but these were unsuccessful. Artificial placing of the atoms to give satisfactory bond lengths was also tried but subsequent refinement always moved them away from chosen positions and in the end it was felt that the least-squares results must be accepted as they stood. However, in spite of this, the bond distances and angles within this molecule are for the most part as expected. Not surprisingly the exceptions involve one of the half-weighted atoms [C(21b)] and it is clear that the block-diagonal refinement has not been able to produce a satisfactory site in this instance. In particular the bond lengths associated with C(21b) (1·14 and 1·72 Å) must be much less accurate than the least-squares standard deviation implies. The short Cl(2)–C(18) distance (1·54 Å) can be brought to an acceptable value (1·72 Å) if an ' independent motion ' correction[11] for the thermal anisotropy is applied [*cf.* the ' normal ' Cl–C(aromatic) distance of 1·70 Å].

The least-squares planes through various sets of atoms in the molecule are given in Table 6 and it is apparent that the ' general ' molecule shows rotation of the benzene rings about the biphenyl pivotal bond. This rotation (16·9°) results from the arrangement of *gauche* ethylene bridges in which C(5) lies −0·733 Å below the plane of benzene ring I (Figure 1) and C(9) +0·794 Å above it. In addition a slight bend in the molecule is observed since there is distinct asymmetry in the deviations of the atoms of one benzene ring from the plane of the other. The pairs of atoms C(14) and C(6), and C(16) and C(8), which respectively lie below and above the plane of the ring defined by C(1)—(3), C(11)—(13), are displaced from it by −0·30, −0·25, 0·40, and 0·45 Å. Moreover C(7), which, if there were no bend should lie in this same plane, deviates from it by 0·12 Å.

TABLE 6

Equations of planes of best fit, referred to orthogonal axes and in the cosine form $Ax + By + Cz + D = 0$, where A, B, and C are the direction cosines. Displacements (Å) of atoms from the planes are given in square brackets

Plane (1): C(1)—(3), C(11)—(13)

$$0{\cdot}236x + 0{\cdot}968y + 0{\cdot}083z - 2{\cdot}766 = 0$$

[C(1) 0·016, C(2) −0·013, C(3) 0·004, C(11) −0·011, C(12) 0·003, C(13) 0·001, Cl(1) −0·050, C(4) 0·040, C(5) −0·733, C(6) −0·254, C(7) 0·124, C(8) 0·445, C(9) 0·794, C(10) −0·044, C(14) −0·300, C(15) 0·033, C(16) 0·397]

Plane (2): C(6)—(8), C(14)—(16)

$$0{\cdot}386x + 0{\cdot}908y - 0{\cdot}163z - 2{\cdot}142 = 0$$

[C(6) 0·005, C(7) −0·005, C(8) 0·001, C(14) −0·002, C(15) −0·001, C(16) 0·002, Cl(1) 0·110, C(1) −0·253, C(2) 0·090, C(3) 0·437, C(4) 0·774, C(5) −0·044, C(9) 0·044, C(10) −0·750, C(11) −0·328, C(12) 0·021, C(13) 0·385]

Plane (3): Cl(2), C(17)—(19), C(22)—(24)

$$0{\cdot}314x - 0{\cdot}554y - 0{\cdot}771z + 8{\cdot}857 = 0$$

[Cl(2) −0·002, C(17) 0·005, C(18) 0·003, C(19) −0·006, C(22) −0·005, C(23) −0·002, C(24) 0·006, C(20) −0·020, C(21a) −0·307, C(21b) 0·492, Cl(2′) −0·002, C(17′) −0·010, C(18′) −0·008, C(19′) 0·001, C(20′) 0·016, C(21a′) 0·303, C(21b′) −0·497 (C22′) 0·000, C(23′) −0·003, C(24′) −0·010]

Interplanar angles: (1)–(2) 16·9°

An obvious contrast with the ' general ' molecule is seen in the near-planarity of the ' disordered ' conformer. This suggests immediately that the torsional angle must be close to zero and in gross terms the differences between the two molecules are so explained. An associated effect is found in the relative conformations of the ethylene bridges. They can be described as having the δδ (or λλ) * conformation in the ' general ' molecule and the δλ conformation in the other.

This idealized situation is modified in the ' disordered ' molecule in much the same way as previously noted for the ' general ' conformer as can be seen when the observed displacements of C(20), C(21a), and C(21b) from plane (3) (see Table 6) are considered. If these atoms were symmetrically displaced above and below the mean plane they would presuppose not only the zero torsional angle but also a small molecular ' step ' such that the two benzene rings were parallel but not coplanar. Evidence for the ' step ' is lacking although it could well be disguised by the larger thermal parameters derived for the ' disordered ' molecule. On the other hand, evidence for some degree of rotation about the central carbon–carbon bond is seen in the asymmetrical displacement of the bridging atoms; two lie approximately in the mean molecular plane but the other two are removed from it. This situation is shown in Figure 2 which also indicates how the ' disordered ' molecule obtained from the refinement reflects the superposition of two conformers which are identical or nearly so. A value for the torsional angle in the ' disordered ' molecule cannot be given but it certainly must be small since the displacements from biphenyl coplanarity which it produces are hidden by the derived thermal parameters.

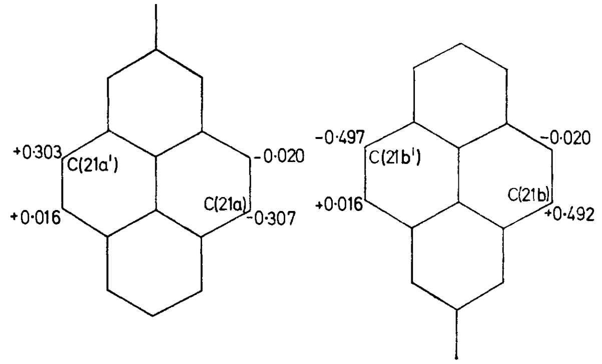

FIGURE 2 ' Disordered ' molecule showing the relative positions of the ethylene bridge carbon atoms in each member of the superposed part with respect to plane (3) (Table 6)

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* See Report of the Commission on the Nomenclature of Inorganic Chemistry of I.U.P.A.C., *Inorg. Chem.*, 1970, **9**, 1.

[11] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

This analysis has shown that, in the solid state at least, two conformations of the molecule of (I) can exist simultaneously, the major difference between them lying only in their relative torsional angles and ethylene bridge positions. In solution, where the torsional angle is believed to be close to zero,[5,8] it appears that the δλ conformer described by the ' disordered ' molecule is favoured but on crystallization some molecules take the alternative ' general ' conformation. That the δλ conformer exists at all, when it is clearly the more strained in the structural sense, testifies to the resonance stabilisation which must occur in this molecule.

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