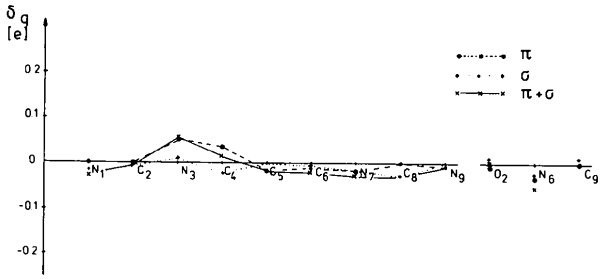

Fig. 7. Changes in electronic structure of the 9-methylisoguanine cation after ion-pair formation with Cl^-.

9-Methylisoguanine hydrochloride possesses a dipole moment of 19·9 D and therefore must interact strongly with other molecules. In the crystal structure, two 9-methylisoguanine hydrochloride ion pairs are related by an inversion centre to form a base pair such that the dipole moments cancel each other.

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On the Disorder in the Crystal Structure of *trans*-Tetrachlorostilbene

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The crystal structure of *trans*-tetrachlorostilbene [Norrestam, Hovmöller, Palm, Göthe & Wachtmeister (1977), *Acta Cryst.* B33, 370–376] has been reinvestigated by means of a completely disordered model in which each atom is distributed equally over two positions. This model, refined to an R value of 5·3%, does not violate the stacking of molecules.

Introduction

Recently, Norrestam, Hovmöller, Palm, Göthe & Wachtmeister (1977) reported the crystal structures of the *cis* and *trans* isomers of tetrachlorostilbene [1,2-bis(4-chlorophenyl)-1,2-dichloroethylene]. The *trans* isomer is centrosymmetric and crystallizes with two molecules in the space group $P2_1/c$. The authors observed disorder in the structure of the *trans* isomer. This disorder was approximated by including C(α) with equal occupancy in two positions (see Fig. 1; consult also their Fig. 2). The second position for C(α) is obtained from the first by rotating the central ethylene bond through 80° about the normal of the ethylene plane. The occupancy for both positions is 0·5. Although this model could be refined to an R value of 4·3% using 854 significant reflexions the resulting geometry is unacceptable chemically: the valency angles C(2)–C(1)–C(α) and C(6)–C(1)–C(α) (122·4 and 115·4°) differ by the large amount of 7°, while C(α) is separated by a distance of 0·44 Å from the least-squares plane of the benzene ring.

Refinement with constraints

Inspection of Fig. 1 reveals the possibility of introducing a chemically acceptable model in which each atom [with the possible exceptions of Cl(α) and C(4)] is distributed over two positions. Using the reflexion data set of Norrestam *et al.* and introducing their positional parameters (disregarding H atoms) with isotropic temperature factors, an R value of 14% was obtained: the resulting difference Fourier map clearly showed maxima collinear with the input positions at distances 0·66 and −0·63 Å for C(1), 0·65 and −0·57 Å for C(6) and 0·65 Å for C(2). A reasonable explanation of these maxima can only be given in terms of a disordered structure. However, we know from past experience that it is impossible to refine such a model by conventional least squares.

To make least-squares refinement possible the following slack constraints were introduced: (1) planar phenyl rings with collinear C(α)–C(1) and C(4)–Cl(4) bonds; (2) bond distances of about 1·39 Å in the benzene ring, 1·70 Å for C(α)–Cl(α) and C(4)–Cl(4), 1·34 Å for the central C–C bond and 1·50 Å for C(α)–C(1); (3) reasonable exocyclic valency angles not deviating more than 2° from 120°. We used a least-squares program with slack constraints (Waser, 1963), constraining 1–2 distances (bond lengths), 1–3 distances (valency angles) and 1–4 distances in order to maintain planar benzene rings. An account of this procedure applied to the structure of $(C_7H_{13}COO)_2$-Ca.$5H_2O$ has been given (Flapper, Verschoor, Rutten & Romers, 1977).

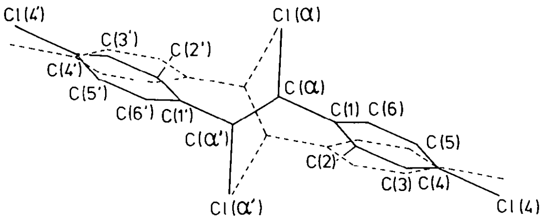

Fig. 1. A disordered model of molecules *A* (full lines) and *B* (broken lines) of *trans*-tetrachlorostilbene. The numbering of the atoms (adapted from Norrestam *et al.*) of molecule *A* is indicated. The atoms generated by inversion are indicated by primes.

During the refinement it became clear that *all* atoms are disordered. The H atoms were kept at calculated

Table 1. *Fractional coordinates*

	x	*y*	*z*
Cl(α*A*)	−0·0550	0·0050	0·2715
Cl(4*A*)	0·5812	0·3650	0·1384
C(1*A*)	0·1818	0·1109	−0·0025
C(2*A*)	0·3912	0·1024	0·0871
C(3*A*)	0·5136	0·1807	0·1361
C(4*A*)	0·4276	0·2674	0·0939
C(5*A*)	0·2217	0·2758	−0·0009
C(6*A*)	0·0994	0·1975	−0·0501
C(α*A*)	0·0504	0·0254	−0·0581
Cl(α*B*)	−0·0644	−0·0001	0·2697
Cl(4*B*)	0·5984	0·3647	0·0846
C(1*B*)	0·1745	0·1098	0·0634
C(2*B*)	0·3913	0·1082	0·1417
C(3*B*)	0·5234	0·1868	0·1404
C(4*B*)	0·4356	0·2679	0·0672
C(5*B*)	0·2151	0·2707	−0·0027
C(6*B*)	0·0849	0·1916	−0·0054
C(α*B*)	0·0282	0·0252	0·0714
H(2*A*)	0·4525	0·0424	0·1202
H(3*A*)	0·6688	0·1765	0·1853
H(5*A*)	0·1606	0·3367	−0·0396
H(6*A*)	−0·0492	0·2022	−0·1155
H(2*B*)	0·4510	0·0496	0·1944
H(3*B*)	0·6730	0·1848	0·2074
H(5*B*)	0·1552	0·3292	−0·0451
H(6*B*)	−0·0681	0·1945	−0·0555

Table 2. *Bond distances* (Å), *valency angles* (°) *and torsion angles* (°)

The bond distances of the aromatic rings are 1·388 or 1·387 Å, the valency angles are 120·0 or 119·9°.

	A	*B*		*A*	*B*
C(1)–C(α)	1·512	1·513	C(2)–C(1)–C(α)	119·8	119·7
C(α)–C(α')	1·335	1·335	C(6)–C(1)–C(α)	120·1	119·9
C(α)–Cl(α)	1·690	1·694	C(1)–C(α)–C(α')	121·4	121·5
C(4)–Cl(4)	1·708	1·710	C(1)–C(α)–Cl(α)	116·0	116·4
			C(α')–C(α)–Cl(α)	122·6	122·0
			C(3)–C(4)–Cl(4)	121·3	118·0
			C(5)–C(4)–Cl(4)	118·4	121·8

	A	*B*
C(2)–C(1)–C(α)–C(α')	74·7	−109·9
C(6)–C(1)–C(α)–C(α')	−109·1	76·9
C(1)–C(α)–C(α')–Cl(α')	4·4	−1·3
C(α)–C(1)–C(2)–C(3)	179·1	−177·6
C(α)–C(1)–C(6)–C(5)	−179·1	175·9
Cl(4)–C(4)–C(5)–C(6)	175·5	−176·4
Cl(4)–C(4)–C(3)–C(2)	−175·4	175·0

Aromatic rings	*A*	*B*		*A*	*B*
C(1)–C(2)	2·9	−4·3	C(4)–C(5)	1·5	−2·4
C(2)–C(3)	−0·6	2·6	C(5)–C(6)	0·8	0·7
C(3)–C(4)	−1·6	0·8	C(6)–C(1)	−3·0	2·7

positions and were not refined; their isotropic temperature parameters were allowed to vary yielding values between 3·9 and 5·1 Å^2. The heavy atoms were refined anisotropically. Futhermore, the temperature parameters of corresponding atoms in molecules *A* and *B* were kept equal during the refinement. During the final stage we inspected the ratio of *A* to *B* molecules and obtained the value 50·05/49·93. The final conventional *R* value is 5·28%.* The positional parameters are listed in Table 1. The geometry presented (Table 2) demonstrates that the input model remained stable during refinement. No standard deviations are given, for obvious reasons. The symmetry of the refined disordered model is $2/m$.†

No exceptionally short intermolecular distances can be detected in the ordered or the disordered structures. Surprisingly the shortest $H\cdots H$ distance (2·32 Å) is found between molecules *A* [involving H(2*A*) and H(2′*A*)]. All other $H\cdots H$ distances are longer than 2·52 Å. Since, moreover, all $C\cdots H$ distances are longer than 2·83 Å and interatomic distances between the heavy atoms are longer than 3·4 Å we conclude that the disordered model proposed does not violate packing requirements. This result is a reminder to regard with caution unexpected geometrical results obtained by refinement of structures containing disorder.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33452 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† A better input model with endocyclic bond angles at C(1) and C(4) of about 118 and 121° might have been considered. Such a model would agree with observed distortions of *para*-substituted phenyl rings (Domenicano, Vaciago & Coulson, 1975*a*,*b*). The main purpose of our paper is, however, to demonstrate the total disorder in the structure of the title compound which inhibits presentation of a detailed geometry.

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Die Kristallstruktur eines Ethenotripyrrens, einem Vertreter einer neuen Klasse von Polymethinfarbstoffen

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The blue dye-stuff 3,3′,3″,5,5″-pentamethyltripyrro-2,2′-methene-5′,2″-ethene hydrochloride hydrate, $[C_{20}H_{24}N_3]^+Cl^-.H_2O$, crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 27·936\ (10)$, $b = 9·675\ (4)$, $c = 7·750\ (4)$ Å, $\beta = 106·83\ (3)°$, $Z = 4$. On an automatic single-crystal diffractometer 3797 independent reflexions were measured using Cu $K\alpha$ radiation. The structure was solved by direct methods. The least-squares refinement yielded a final *R* index of 0·059 for 1986 observed reflexions. The dye cation belongs to the dye-stuff class of polymethines. It is almost planar, allowing a polymethine type of π resonance. Besides the conformation of the cation the bond-length–bond-order correlation is discussed using resonance formulas and quantum-mechanical calculations. In the crystal structure the dye cations build up parallel sheets with an average separation of 3·33 Å, allowing π interaction between them. A building block of the crystal structure is a centrosymmetric 'dimer' formed by hydrogen bridges linking two formula units.

Einleitung

Seit langer Zeit war bekannt, dass sich Pyrromethene (I*a*,*b*,*c*) unter deutlichen Farbänderungen zersetzen (Fischer & Orth, 1937). Doch erst in jüngster Zeit konnten einige der diesen Farbänderungen zugrundeliegenden Farbstoffe isoliert werden. So erhielt man (Treibs, Strell, Strell, Grimm, Gieren & Schanda, 1978) durch Erhitzen von (I*a*) in methanolischer Lösung ein instabiles gelbes Zwischenprodukt, welches sich beim