References

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.

Conant, J. W., Cady, H. H., Ryan, R. R., Yarnell, J. L. & Newsam, J. M. (1979). *The Atom Positions of Pentaerythritol Tetranitrate* (*PETN*, $C_5H_8N_4O_{12}$) *Determined by X-ray and by Neutron Diffraction*. Report LA-7756-MS. Los Alamos National Laboratory, New Mexico, USA.

Eilerman, D. & Rudman, R. (1979). *Acta Cryst.* B35, 2458–2460.

Goodwin, T. H. & Hardy, R. (1938). *Proc. R. Soc. London Ser. A*, **164**, 369–383.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Klyne, W. & Prelog, V. (1960). *Experientia*, **16**, 521–523.

Lapp, R. L. & Jacobson, R. A. (1979). *ALLS. A Generalized Crystallographic Least-Squares Program.* Ames Laboratory (DOE) and Iowa State Univ., Ames, Iowa, USA.

Main, P., Woolfson, M. M. & Germain, G. (1976). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Moore, J. C. & Palmer, R. A. (1991). *J. Crystallogr. Spectrosc. Res.* **21**, 601–614.

Powell, D. R. & Jacobson, R. A. (1980). *FOUR. A Generalized Fourier Program.* Ames Laboratory (DOE) and Iowa State Univ., Ames, Iowa, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Tieghi, G. & Zocchi, M. (1972). *Cryst. Struct. Commun.* **1**, 167–171.

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(*Z*)-Perchlorostilbene

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Abstract

Steric repulsion of the bulky Cl atoms causes the perchlorophenyl rings to rotate out of the plane of the central double bond eliminating the conjugation between the three π systems. Molecules pack as interlocking dimers and the dimeric pairs adhere by face-to-face π stacking.

Comment

Sterically congested stilbenes (Gano, Park, Subramaniam, Lenoir & Gleiter, 1991; Gano, Park, Pinkerton & Lenoir 1990, 1991; Gano, Subramaniam & Birnbaum, 1990) and the effect that steric congestion has on (*Z*)/(*E*)-isomerization barriers (Gano, Lenoir, Park & Roesner, 1987) have been of some interest to us. Our attention was drawn to the very high isomerization barrier reported for (*Z*)-perchlorostilbene (Ballester & Rosa, 1960), a member of the large class of known perchloroarenes (Ballester, 1989). Alternative explanations for the observed results based on our earlier work prompted an X-ray structural determination of this molecule to verify the structure and reveal the geometry. The original structural assignment for (*Z*)-perchlorostilbene is confirmed and a highly twisted geometry is demonstrated.

The structure of (*Z*)-perchlorostilbene was calculated using force-field programs (*PCModel* with and without the *PI* option; Gilbert & Gyjewski, 1992) and semi-empirical programs (*MOPAC* with the *AM*1 and *PM*3 parameter sets; Dewar, Zoebisch, Healy & Stewart, 1985; Stewart, 1989). All programs gave the same general structure. The force-field calculation which included a *PI* contribution, *MMX*(*PI*), gave the best fit and showed no major faults in its structure. The simple force-field program *MMX* greatly underestimated the out-of-plane twisting of the phenyl groups. This failure reoccurs with twisted π systems using this approach. Surprisingly, the semi-empirical programs fail to predict the twist about the central double bond.

The structure of (*Z*)-perchlorostilbene is shown in Fig. 1 and some selected structural features are noted in Table 3. The central double bond is twisted 6.4 (3)°, based on the Cl atoms, or -11.5 (5)° based on the phenyl groups. The phenyl rings are rotated out of the plane of the double bond by, on average, 76° each, preventing the strong conjugation of the three π systems, as would have occurred had the system been planar. The bond length $C_{sp^2}{=}C_{sp^2}$ of 1.336 (3) Å is typical for the C=C—C_{ar} system (1.339 Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), but the average value of the single bond, 1.484 (3) Å, is closer to that observed in *o*-biphenyls (1.487 Å) than in the conjugated C=C—C_{ar} system (1.470 Å; Allen *et al.* 1987). The slightly shortened C_{sp^2}—Cl bonds of average length 1.727 (2) Å, compared with 1.734 Å (Allen *et al.*, 1987), indicates the involvement of the vicinal Cl atoms in the electronic interactions and support its similarity to *o*-biphenyls. A similar arrangement of the pentachlorophenyl rings has been observed in perchloro-1,2,3-triphenylnaphthalene (Gali, Solans, Miravitlles, Font-Altaba & Armet, 1978), where the perchlorophenyls are rotated out of the plane defined by the C—C—C—C fragment of the naphthalene ring by an average of 73°. The twist of the aromatic rings allows the molecule to adopt a 'staggered' rather than 'eclipsed' conformation (see the Newman projection, Fig. 1*b*) as is observed in the overcrowded sandwich-type molecules like ferrocenes and ferrocenophanes (Kaluski & Skrzypczak-Jankun, 1978), where the distance and dihedral angle between the aromatic moieties is much smaller. In this case, the three-dimensional arrangement of the molecules in the crystal seems to be an important factor.

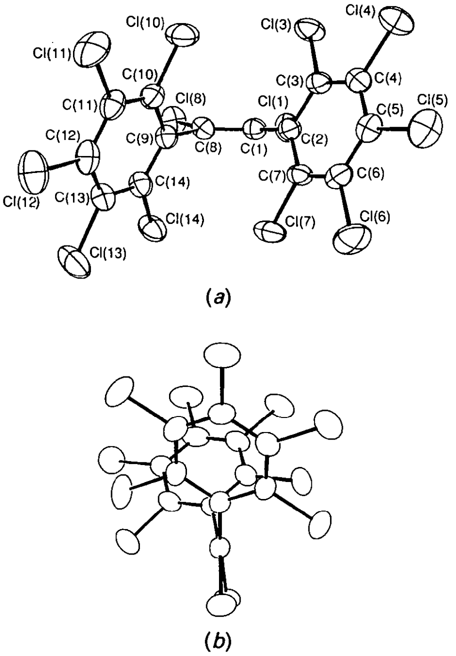

Fig. 1. (*a*) Front view of (*Z*)-perchlorostilbene showing atom labeling and 50% probability thermal ellipsoids. (*b*) Newman projection of (*Z*)-perchlorostilbene viewed along the central double bond.

The packing diagram for (*Z*)-perchlorostilbene is shown in Fig. 2. The (*Z*)-perchlorostilbene units appear as pairs fitting together at opposing phenyl rings like two interlocked clamshells. These pairs are then associated with one another through a face-to-face π stacking interaction. The χ^2 values associated with the mean least-squares planes calculated for the phenyl rings are 44 for C(2)–C(7) and 235 for C(9)–C(14), showing that the aromatic rings are not strictly planar. The planarity of the phenyl ring C(9)–C(14) engaged in the face-to-face interaction is more disturbed than for the C(2)–C(7) ring that is close to its symmetry mate and also involved in the face-to-edge interaction with the C(9)–C(14) pentachlorophenyl of another molecule. The distances between the planes of the parallel C(9)–C(14) and C(2)–C(7) pairs are 3.7 and 3.3 Å, respectively. The shortest intermolecular contact in the face-to-face interaction is Cl(4)···Cl(7) at 3.365 (1) Å; the shortest contact in the face-to-edge interaction is Cl(12)···C(5) at 3.384 (2) Å. Face-to-face and face-to-edge orientations of aromatic fragments are frequently observed in proteins, as a stabilizing factor in their tertiary structure. The Cl substituents are significantly out of the plane of the phenyl ring with Cl(7) and Cl(4) being most affected. The mean C_{ar}—Cl distance of 1.716 (5) Å agrees well with the value of 1.722 Å calculated for 81 such bonds in the other pentachlorophenyls (Miratvitlles, Molins, Solans, Germain & Declercq, 1985; Pedersen, 1975; Veciana, Carilla, Miratvitlles & Molina, 1987; Armet *et al.*, 1987; Wang, Chen, Xu, Zhang, Pan & Tang, 1987; Gali *et al.*, 1978).

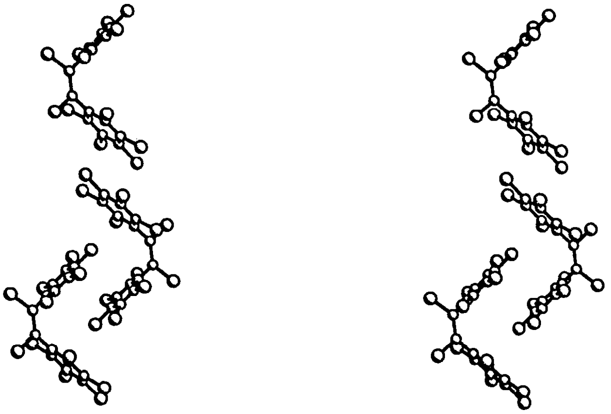

Fig. 2. View of (*Z*)-perchlorostilbene along the (100) axis showing the packing of molecules in the crystal.

Experimental

Crystal data

$C_{14}Cl_{12}$
M_r = 593.59
Triclinic
$P\bar{1}$
a = 8.961 (1) Å
b = 8.979 (2) Å
c = 13.920 (2) Å
α = 91.12 (2)°
β = 97.66 (1)°
γ = 114.75 (2)°
V = 1004.5 (3) Å^3
Z = 2.00
D_x = 1.96 Mg m^{-3}
D_m = 1.980 Mg m^{-3}
Density measured by flotation

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 15 reflections
θ = 10–14°
μ = 1.667 mm^{-1}
T = 294 K
Prism
0.30 × 0.26 × 0.10 mm
Yellow
Crystal source: prepared as described by Molinet (1955); recrystallized from dichloromethane

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4097 measured reflections
3925 independent reflections
3338 observed reflections [$I > 3.0\sigma(I)$]

R_{int} = 0.015
θ_{max} = 25.97°
$h = -11 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity variation: −8.08%

Refinement

Refinement on F
Final R = 0.040
wR = 0.055
S = 1.920
3338 reflections
235 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.4798 e Å^{-3}
$\Delta\rho_{\min}$ = −0.1558 e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.36 × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: CAD-4 (Enraf-Nonius, 1977). Cell refinement: CAD-4. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: Direct methods (*MULTAN*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN CIFIN*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl(1)	0.80933 (9)	0.06940 (8)	−0.06665 (5)	0.0478 (2)
Cl(3)	0.39723 (7)	−0.10851 (8)	−0.13690 (6)	0.0500 (2)
Cl(4)	0.15649 (8)	−0.4611 (1)	−0.09982 (6)	0.0579 (2)
Cl(5)	0.2727 (1)	−0.74219 (9)	−0.09849 (6)	0.0592 (2)
Cl(6)	0.62375 (9)	−0.67316 (8)	−0.14312 (6)	0.0634 (2)
Cl(7)	0.87013 (8)	−0.31858 (9)	−0.17096 (6)	0.0614 (2)
Cl(8)	0.89555 (8)	0.20727 (8)	−0.26397 (5)	0.0471 (2)
Cl(10)	0.43587 (8)	−0.1233 (1)	−0.37723 (6)	0.0556 (2)
Cl(11)	0.3789 (1)	−0.3259 (1)	−0.57223 (6)	0.0661 (3)
Cl(12)	0.6639 (1)	−0.4033 (1)	−0.63127 (5)	0.0690 (3)
Cl(13)	1.00689 (9)	−0.2681 (1)	−0.49813 (6)	0.0679 (2)
Cl(14)	1.07287 (7)	−0.0405 (1)	−0.31417 (5)	0.0515 (2)
C(1)	0.7362 (3)	−0.0591 (3)	−0.1730 (2)	0.0347 (6)
C(2)	0.6208 (3)	−0.2304 (3)	−0.1600 (2)	0.0331 (6)
C(3)	0.4600 (3)	−0.2650 (3)	−0.1410 (2)	0.0355 (6)
C(4)	0.3520 (3)	−0.4219 (3)	−0.1230 (2)	0.0380 (7)
C(5)	0.4034 (3)	−0.5476 (3)	−0.1228 (2)	0.0377 (7)
C(6)	0.5614 (3)	−0.5170 (3)	−0.1411 (2)	0.0401 (7)
C(7)	0.6698 (3)	−0.3585 (3)	−0.1579 (2)	0.0367 (6)
C(8)	0.7811 (3)	−0.0005 (3)	−0.2572 (2)	0.0346 (6)
C(9)	0.7477 (3)	−0.1023 (3)	−0.3498 (2)	0.0341 (6)
C(10)	0.5940 (3)	−0.1641 (3)	−0.4104 (2)	0.0379 (7)
C(11)	0.5681 (3)	−0.2547 (3)	−0.4976 (2)	0.0429 (8)
C(12)	0.6945 (4)	−0.2882 (3)	−0.5248 (2)	0.0457 (8)
C(13)	0.8500 (3)	−0.2265 (3)	−0.4662 (2)	0.0422 (7)
C(14)	0.8758 (3)	−0.1301 (3)	−0.3809 (2)	0.0392 (7)

Table 2. *Bond lengths* (Å) *and angles* (°)

Cl(1)—C(1)	1.730 (2)	C(2)—C(3)	1.404 (4)
Cl(3)—C(3)	1.721 (3)	C(2)—C(7)	1.392 (4)
Cl(4)—C(4)	1.714 (3)	C(3)—C(4)	1.386 (3)
Cl(5)—C(5)	1.718 (2)	C(4)—C(5)	1.386 (4)
Cl(6)—C(6)	1.714 (3)	C(5)—C(6)	1.385 (4)
Cl(7)—C(7)	1.713 (3)	C(6)—C(7)	1.393 (3)
Cl(8)—C(8)	1.724 (2)	C(8)—C(9)	1.486 (3)
Cl(10)—C(10)	1.720 (3)	C(9)—C(10)	1.396 (3)
Cl(11)—C(11)	1.720 (3)	C(9)—C(14)	1.392 (4)
Cl(12)—C(12)	1.712 (3)	C(10)—C(11)	1.384 (4)
Cl(13)—C(13)	1.707 (3)	C(11)—C(12)	1.383 (5)
Cl(14)—C(14)	1.724 (2)	C(12)—C(13)	1.395 (4)
C(1)—C(2)	1.482 (3)	C(13)—C(14)	1.390 (4)
C(1)—C(8)	1.336 (3)		
Cl(1)—C(1)—C(2)	113.8 (2)	Cl(8)—C(8)—C(1)	120.6 (2)
Cl(1—C(1)—C(8)	120.4 (2)	Cl(8)—C(8)—C(9)	114.1 (2)
C(2)—C(1)—C(8)	125.8 (2)	C(1)—C(8)—C(9)	125.2 (2)
C(1)—C(2)—C(3)	119.8 (2)	C(8)—C(9)—C(10)	122.4 (3)
C(1)—C(2)—C(7)	122.3 (2)	C(8)—C(9)—C(14)	119.4 (2)
C(3)—C(2)—C(7)	117.7 (2)	C(10)—C(9)—C(14)	118.0 (2)
Cl(3)—C(3)—C(2)	119.4 (2)	Cl(10)—C(10)—C(9)	119.3 (2)
Cl(3)—C(3)—C(4)	119.2 (2)	Cl(10)—C(10)—C(11)	119.6 (2)
C(2)—C(3)—C(4)	121.4 (3)	C(9)—C(10)—C(11)	121.1 (3)
Cl(4)—C(4)—C(3)	120.5 (2)	Cl(11)—C(11)—C(10)	120.2 (2)
Cl(4)—C(4)—C(5)	119.8 (2)	Cl(11)—C(11)—C(12)	119.8 (2)
C(3)—C(4)—C(5)	119.6 (2)	C(10)—C(11)—C(12)	120.0 (2)
Cl(5)—C(5)—C(4)	120.4 (2)	Cl(12)—C(12)—C(11)	120.7 (2)
Cl(5)—C(5)—C(6)	119.5 (2)	Cl(12)—C(12)—C(13)	119.0 (3)
C(4)—C(5)—C(6)	120.2 (2)	C(11)—C(12)—C(13)	120.2 (2)
Cl(6)—C(6)—C(5)	120.2 (2)	Cl(13)—C(13)—C(12)	120.9 (2)
Cl(6)—C(6)—C(7)	120.0 (2)	Cl(13)—C(13)—C(14)	120.2 (2)
C(5)—C(6)—C(7)	119.8 (3)	C(12)—C(13)—C(14)	119.0 (3)
Cl(7)—C(7)—C(2)	119.4 (2)	Cl(14)—C(14)—C(9)	119.8 (2)
Cl(7)—C(7)—C(6)	119.3 (2)	Cl(14)—C(14)—C(13)	118.6 (2)
C(2)—C(7)—C(6)	121.3 (2)	C(9)—C(14)—C(13)	121.6 (2)

Table 3. *Measured and calculated structure values* (Å, °) *for (Z)-perchlorostilbene*

	X-ray	*MMX*	*MMX*(*PI*)	*AM*1	*PM*3
Cl(8)—C(8)—C(l)—Cl(1)	6.41	18.6	10.62	1.84	0.89
C(7)—C(2)—C(l)—C(8) or C(10)—C(9)—C(8)—C(1)	78.4 80.6	24.4 25.6	71.2 73.0	74.1 75.5	77.7 78.7
C(l)—C(8)	1.336	1.363	1.352	1.351	1.344
Cl(1)—C(1) or Cl(8)—C(8)	1.724 1.730	1.757	1.746	1.701	1.688
C(2)—C(l)—C(8) or C(1)—C(8)—C(9)	125.5 125.2	127.7	125.2	125.4	125.7
Cl(1)—C(1)—C(8) or Cl(8)—C(8)—C(1)	120.4 120.6	115.8	121.2	121.0	119.7

A crystal of (*Z*)-perchlorostilbene was mounted on a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement. The data were collected at room temperature; the backgrounds were obtained by analysis of the scan profile (Blessing, Coppens & Becker, 1974). A linear decay correction was applied (from 1.000 to 1.043 on I). The agreement factors for the averaging of the 306 reflections were 1.4% based on intensity and 1.3% based on F_o. The structure was solved using direct methods (Main *et al.*, 1980) and was refined by full-matrix least-squares methods where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$. Anomalous dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f_o and f_c were those of Cromer & Waber (1974). Only reflections having intensities greater than 3.0 times their standard deviation and acceptable $w(\Delta F)^2$ were used in the refinements. Seven points were rejected on the basis of the latter criterion. The errors of maxima and minima in the final difference Fourier were estimated at 0.09, based on ΔF (Cruickshank, 1949). The analysis of statistical data based on the collection, sinθ/λ, and various classes of indices showed no unusual trends. All X-ray calculations were performed on a MicroVAX 3100 computer using *MolEN* (Fair, 1990).

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Lists of structure factors, anisotropic thermal parameters, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71365 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1067]

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1-S19.

Armet, O., Veciana, J., Roveria, C., Riera, J., Castaner, J., Molina, E., Rius, J., Miravitlles, C., Olivella, S. & Brichfeus, J. (1987). *J. Phys. Chem.* **91**, 5608-5616.

Ballester, M. (1989). *Adv. Phys. Org. Chem.* **25**, 267.

Ballester, M. & Rosa, J. (1960). *Tetrahedron*, **9**, 156-162.

Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488-492.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 154-157.

Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902-3909.

Enraf-Nonius (1977). *CAD-4 Operations Manual.* Enraf-Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf-Nonius, Delft, The Netherlands.

Gali, S., Solans, X., Miravitlles, C., Font-Altaba, M. & Armet, O. (1978). *Acta Cryst.* **B34**, 1011-1014.

Gano, J. E., Lenoir, D., Park, B.-S. & Roesner, R. A. (1987). *J. Org. Chem.* **52**, 5636-5638.

Gano, J. E., Park, B.-S., Pinkerton, A. A. & Lenoir, D. (1990). *J. Org. Chem.* **55**, 2688-2693.

Gano, J. E., Park, B. S., Pinkerton, A. A. & Lenoir, D. (1991). *Acta Cryst.* **C47**, 162-164.

Gano, J. E., Park, B.-S., Subramaniam, G., Lenoir, D. & Gleiter, R. (1991). *J. Org. Chem.* **56**, 4806-4808.

Gano, J. E., Subramaniam, G. & Birnbaum, R. (1990). *J. Org. Chem.* **55**, 4760-4763.

Gilbert, K. & Gyjewski, J. (1992). *PCModel for the Macintosh.* Version 4.0. Serena Software, Bloomington, Indiana, USA.

Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781-782.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kaluski, Z. & Skrzypczak-Jankun, E. (1978). *Proceedings of the Pre-Congress Symposium on Organic Crystal Chemistry*, pp. 273-293. Poznań: Dymaczewo.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Miravitlles, C., Molins, E., Solans, X., Germain, G. & Declercq, J.-P. (1985). *J. Incl. Phenom. Mol. Recognit. Chem.* **3**, 27-34.

Molinet, C. (1955). MS thesis, Univ. of Madrid, Spain.

Pedersen, B. F. (1975). *Acta Cryst.* **B31**, 2931-2933.

Stewart, J. J. (1989*a*). *J. Comput. Chem.* **10**, 209-220, 221-264.

Veciana, J., Carilla, J., Miravitlles, C. & Molina, E. (1987). *J. Chem. Soc. Chem. Commun.* pp. 812-814.

Wang, T.-L., Chen, J.-B., Xu, W.-H., Zhang, S.-W., Pan, Z.-H. & Tang, Y.-Q. (1987). *Acta Chim. Sin.* **45**, 636-644.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139-1144.

Acta Cryst. (1993). C**49**, 1988–1990

1,2,4-Trifluoro-6,8-dimethyl-3-trifluoromethylphenazine, $C_{15}H_8F_6N_2$, Produced *via* Thermolysis of Perfluoro-4-azidotoluene in the Presence of 2,4,6-Trimethylaniline

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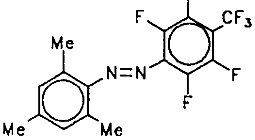
Abstract

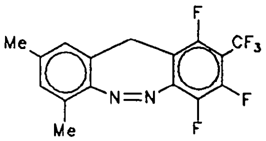
Despite extensive substitution, the dimensions of the planar phenazine rings remain very close to those of the unsubstituted molecule [Woźniak, Kariuki & Jones (1991). *Acta Cryst.* C**47**, 1113-1114]. Typically, the molecules form stacks in which fluorinated rings overlap methylated rings of adjacent molecules.

Comment

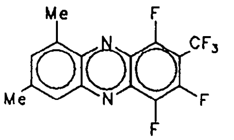
The structure determination was undertaken to establish beyond doubt the identity of unexpected products encountered during an extension (Banks & Madany, 1993) of studies on the trapping of thermally generated perfluoroaryl nitrenes with 1,3,5-trimethylbenzene (Banks & Madany, 1985) and aniline (Banks & Prakash, 1974). Formation of the azo compound (1) can be ascribed to trapping of the incipient singlet nitrene 4-$CF_3C_6F_4N$ by the electron-rich 2,4,6-trimethylaniline (Banks & Prakash, 1974). The dibenzo[1,2]diazepine (2) is known to be produced *via* the thermal intramolecular dehydrofluorination of (1) (Alty, Banks, Fishwick, Pritchard & Thompson, 1984). However, just how the phenazine (3) arises is not clear. Thermal oxidative cyclization of non-fluorinated azobenzenes to phenazines in the presence of ferrous oxalate has been reported (Abramovitch & Davis, 1968), but



(1)



(2)



(3)