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The Stereoconfiguration and Restrained Refinement of an Unsymmetric Trimer: 3,7,11-Tris(p-chlorophenyl)-2,3,6,7,10,11-hexahydro-2,2,6,6,10,10-hexaphenyltris[1,2,4]triazolo[1,5-*a*:1',5'-*c*:1'',5''-*e*][1,3,5]triazine: $C_{60}H_{42}Cl_3N_9$

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Abstract

C,C,N^{α}-triaryl-N^{β}-cyanoazomethine imines trimerize on heating in solution or even in the crystalline state. An X-ray single-crystal analysis was performed on one of these trimers to determine whether or not the molecule has threefold symmetry. Results of the study showed the trimer to be unsymmetric. The compound $(C_{60}H_{42}Cl_3N_9)$ crystallizes in the triclinic space group $I\bar{1}$ with $a = 16\cdot102$ (10), $b = 24\cdot894$ (20), $c = 13\cdot241$ (9) Å, $\alpha = 96\cdot7$ (1), $\beta = 91\cdot2$ (1), $\gamma = 106\cdot8$ (1)°, $Z = 4$ [reduced Niggli cell: $P\bar{1}$, $a = 13\cdot242$, $b = 13\cdot558$, $c = 16\cdot103$ Å, $\alpha = 108\cdot5$, $\beta = 91\cdot2$, $\gamma = 111\cdot6°$, $Z = 2$; transformation matrix: (001 $\overline{111}$ $\overline{122}$·$\overline{1}00$)], $D_x = 1\cdot312$ g cm^{-3} and $\mu = 2\cdot36$ cm^{-1}. The structure was solved by direct methods and refined both by full-matrix and restrained least-squares procedures. A full-matrix refinement using 4003 reflections and only the non-hydrogen atoms gave a final R_w of 0·072. An anisotropic restrained least-squares refinement, using all the atoms and all 6053 reflections, gave a final R_w of 0·065.

Introduction

C,C,N^{α}-triaryl-N^{β}-cyanoazomethine imines (*e.g.* I) trimerize on heating in solution or even in the crystalline state to give products such as (II) {3,7,-11-tris(*p*-chlorophenyl)-2,3,6,7,10,11-hexahydro-2,2,-6,6,10,10-hexaphenyltris[1,2,3]triazolo[1,5-*a*:1',5'-*c*:1'',5''-*e*][1,3,5]triazine}. The tetracyclic heterosystem is formed by a sequence of three 1,3-dipolar cyclo-

addition reactions of the azomethine imine to the cyano group, the first two taking place intermolecularly and the third intramolecularly. The structural formula (II) was correctly predicted in 1962 (Eckell, 1962) and it was suggested that it would have threefold (C_3) molecular symmetry. Studies of spectroscopic data and chemical properties of the compound could not confirm this prediction (Huisgen, Fleischmann & Eckell, 1977). The X-ray study corroborated the structural formula and established the stereochemistry of the molecule. The results of this analysis revealed large departures from C_3 symmetry, with two *p*-chlorophenyl rings projecting away to one side of the average plane of the central heterocyclic ring system and the third $-C_6H_4Cl$ group directed towards the opposite side (Fig. 4).
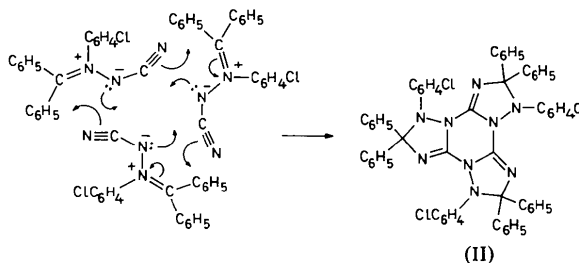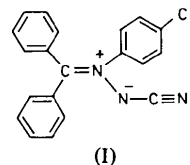

(I)

(II)

Table 1. *Data collection*

Radiation	Mo $K\alpha$ ($\lambda = 0.71069$ Å)
	Zr filter
Data collection	Picker FACS-I at room temperature
Collection technique	θ–2θ scan
Scan width	$1.5° + 2\theta(\alpha_2) - 2\theta(\alpha_1)$
Scan speed	$2.0°$ min^{-1}
Background time	10 s
Maximum $\sin\theta/\lambda$	0.524 Å^{-1}
Number of independent reflections	6053

Experimental

Crystals of (II) were supplied by Professor R. Huisgen of the University of Munich. Table 1 gives a summary of the data collection. Cell dimensions were determined by a least-squares refinement of 12 independently measured reflections (2θ ranging from 18.1–$30.8°$). Data were collected in a non-standard triclinic $I\bar{1}$ cell (rather than $P\bar{1}$) because the crystal was mounted on an axis (a^*) in that cell. Lorentz and polarization corrections were applied and normalized structure factor magnitudes $|E|$ as well as structure factor magnitudes $|F|$ were derived. The structure was solved by the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966). Computer programs written by R. Gilardi and S. A. Brenner of this laboratory were used. All calculations were performed on a Texas Instruments Advanced Scientific Computer.

Refinement

For this molecule, with 114 atoms in the asymmetric unit and over 6000 independent reflections, it was not possible to refine simultaneously all variables with full-matrix methods. Therefore, a refinement procedure incorporating quadratic distance restraints to maintain the local geometry of the mean atomic positions (Konnert, 1976; Hendrickson & Konnert, 1979), as well as restrained anisotropic thermal parameters (Konnert & Hendrickson, 1980), which has already proved to be extremely useful in the refinement of macromolecules (Konnert, 1976; Sielecki, Hendrickson, Broughton, Delbaere, Brayer & James, 1979; Furey, Wang, Yoo & Sax, 1979) was used. The restrained least-squares procedure uses a greatly reduced ('sparse') matrix; shifts in parameters are derived from this matrix not by inversion but by the iterative conjugate gradient method as described by Konnert (1976). For a 100-atom problem the 'sparse' matrix contains approximately 7% of the number of elements needed for a 'full' matrix. Since the trimer contains 114 atoms, it was decided to use restrained least-squares methods for its refinement.

For purposes of comparison, the structure was initially refined using the serial full-matrix least-squares

program *ORXFLS*3 (Busing *et al.*, 1975). Scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). For reasons of economy, the data were restricted to the more significant observations, a subset of 4003 reflections having $|F_o| \geq 5.0$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights (w) were derived from estimated standard deviations of the observed intensities according to Gilardi (1973). H atoms were omitted entirely and only about half the atoms were varied anisotropically in any one cycle (maximum number of variables allowed was 500). Refinement was stopped after four cycles of anisotropic refinement during which the parameters for each atom had been varied at least twice. At that point the standard deviation of an observation of unit weight was 2.76 and the R factors were $R = 7.1$ and $R_w = 7.2\%$. Convergence was slow at this point, and the full-matrix refinement was concluded.

The restrained-refinement program requires the input of a certain amount of stereochemical information to construct the restraint contributions to the residual. Bond distances were restrained by specifying the two atoms involved and a target distance. Angles were restrained (for an angle such as $\angle ABC$ in the group A–B–C) by specifying a target value for the $A \cdots C$ nonbonded distance. In addition, the principal-axes' directions of the thermal ellipsoids were fixed to reduce the number of thermal parameters to three for each atom. These directions are chosen so as to coincide as nearly as possible with expected directions of maximum or minimum displacements (Konnert & Hendrickson, 1980). All of this 'fixed' model information was prepared with the aid of program *MODEL* (Anderson, 1979). Target distances used were arrived at by studying the published values given for several compounds having similar bonding topologies.

The refinement itself was carried out using the restrained-refinement program *CONLSQ* (Konnert, Hendrickson, Flippen-Anderson & Gilardi, 1979). *CONLSQ* operates as described above and will accommodate any space-group symmetry. Restraints on the thermal ellipsoids were applied to the trimer by specifying targets for the variances of the bonded and non-bonded distances (Konnert & Hendrickson, 1980), of $(0.01$ Å$)^2$ and $(0.05$ Å$)^2$. Group-planarity restraints (*i.e.* designated atoms were restrained to remain near the best least-squares plane calculated through them) were applied to each of the phenyl and chlorophenyl rings in the trimer throughout the refinement.

The starting point for the positional parameters for the heavy atoms was the same as the starting point for *ORFLS*. H atoms were inserted in calculated positions. All atoms were initially assigned thermal parameters equivalent to an isotropic B of 4.0 Å^2. During the early refinement cycles all structure factors were given equal weights, approximately equal to the average $|\Delta F|$, since

Table 2. *Fractional coordinates and equivalent iso-tropic thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = (\sum_{R=1}^{3} B_R)/3$ where $B_R = 8\pi^2 U_R^2$. E.s.d.'s were calculated using only the diagonal elements of a least-squares matrix which contained only structure factor contributions.

	x	y	z	B_{eq} (Å²)
Cl	0·1958 (1)	0·7037 (1)	−0·0311 (1)	5·58 (4)
ClA	0·3839 (1)	1·0358 (1)	0·5047 (1)	7·39 (5)
ClB	−0·2759 (1)	0·5875 (1)	0·7498 (1)	6·83 (5)
N(1)	0·0257 (2)	0·7441 (1)	0·4168 (2)	2·54 (9)
N(2)	−0·0005 (2)	0·6940 (1)	0·3445 (2)	2·35 (9)
C(3)	0·0008 (3)	0·6463 (2)	0·4116 (3)	2·49 (11)
N(4)	0·0337 (2)	0·6767 (1)	0·5138 (2)	2·49 (9)
C(5)	0·0402 (3)	0·7283 (2)	0·5124 (3)	2·24 (10)
N(1A)	0·0196 (2)	0·8315 (1)	0·4915 (2)	2·56 (9)
N(2A)	0·0211 (2)	0·8853 (1)	0·4635 (2)	2·45 (9)
C(3A)	−0·0325 (3)	0·8653 (2)	0·3629 (3)	2·63 (11)
N(4A)	−0·0152 (2)	0·8103 (1)	0·3228 (2)	2·49 (9)
C(5A)	0·0072 (2)	0·7930 (2)	0·4029 (3)	2·24 (10)
N(1B)	0·0590 (2)	0·7717 (1)	0·5912 (2)	2·37 (9)
N(2B)	0·0554 (2)	0·7616 (1)	0·6965 (2)	2·35 (9)
C(3B)	0·0743 (3)	0·8234 (2)	0·7470 (3)	2·38 (11)
N(4B)	0·0430 (2)	0·8535 (1)	0·6711 (2)	2·40 (9)
C(5B)	0·0399 (3)	0·8230 (2)	0·5869 (3)	2·24 (10)
C(6)	0·0496 (3)	0·6992 (2)	0·2561 (3)	2·34 (11)
C(7)	0·1240 (3)	0·7415 (2)	0·2492 (3)	3·21 (12)
C(8)	0·1684 (3)	0·7440 (2)	0·1599 (3)	3·56 (13)
C(9)	0·1375 (3)	0·7029 (2)	0·0794 (3)	3·33 (12)
C(10)	0·0616 (3)	0·6612 (2)	0·0825 (3)	4·03 (14)
C(11)	0·0162 (3)	0·6595 (2)	0·1711 (3)	3·65 (13)
C(12)	−0·0921 (3)	0·6107 (2)	0·4216 (3)	2·77 (11)
C(13)	−0·1076 (3)	0·5726 (2)	0·4922 (4)	4·77 (15)
C(14)	−0·1922 (4)	0·5402 (2)	0·5041 (4)	5·65 (17)
C(15)	−0·2593 (3)	0·5452 (2)	0·4477 (4)	5·62 (17)
C(16)	−0·2449 (4)	0·5814 (2)	0·3776 (5)	6·99 (20)
C(17)	−0·1606 (3)	0·6146 (2)	0·3642 (4)	5·51 (17)
C(18)	0·0595 (3)	0·6120 (2)	0·3710 (3)	2·93 (12)
C(19)	0·1461 (3)	0·6301 (2)	0·3993 (4)	4·25 (14)
C(20)	0·2031 (4)	0·6006 (2)	0·3595 (4)	5·74 (17)
C(21)	0·1692 (4)	0·5531 (2)	0·2929 (4)	5·83 (18)
C(22)	0·0844 (4)	0·5331 (2)	0·2652 (4)	6·22 (19)
C(23)	0·0267 (3)	0·5626 (2)	0·3042 (4)	4·94 (16)
C(6A)	0·1098 (3)	0·9200 (2)	0·4630 (3)	2·64 (11)
C(7A)	0·1800 (3)	0·8988 (2)	0·4600 (4)	4·12 (14)
C(8A)	0·2640 (3)	0·9340 (2)	0·4718 (4)	4·86 (15)
C(9A)	0·2767 (3)	0·9913 (2)	0·4863 (4)	4·21 (14)
C(10A)	0·2095 (3)	1·0139 (2)	0·4871 (4)	4·73 (15)
C(11A)	0·1256 (3)	0·9783 (2)	0·4767 (4)	4·00 (14)
C(12A)	−0·1281 (3)	0·8495 (2)	0·3857 (3)	2·97 (12)
C(13A)	−0·1893 (3)	0·8268 (2)	0·3055 (4)	4·40 (15)
C(14A)	−0·2778 (4)	0·8071 (2)	0·3233 (4)	5·24 (16)
C(15A)	−0·3026 (3)	0·8100 (2)	0·4201 (4)	5·53 (17)
C(16A)	−0·2444 (4)	0·8306 (2)	0·5002 (4)	5·85 (18)
C(17A)	−0·1554 (3)	0·8518 (2)	0·4839 (4)	4·47 (15)
C(18A)	−0·0071 (3)	0·9092 (2)	0·2899 (3)	2·61 (11)
C(19A)	−0·0454 (3)	0·9521 (2)	0·2933 (3)	3·75 (14)
C(20A)	−0·0209 (3)	0·9937 (2)	0·2278 (4)	4·45 (14)
C(21A)	0·0392 (3)	0·9908 (2)	0·1596 (4)	4·13 (14)
C(22A)	0·0791 (3)	0·9489 (2)	0·1557 (4)	4·28 (14)
C(23A)	0·0553 (3)	0·9079 (2)	0·2218 (3)	3·49 (13)
C(6B)	−0·0289 (3)	0·7230 (2)	0·7131 (3)	2·58 (11)
C(7B)	−0·0274 (3)	0·6797 (2)	0·7690 (3)	3·63 (13)
C(8B)	−0·1047 (3)	0·6384 (2)	0·7822 (4)	4·32 (14)
C(9B)	−0·1798 (3)	0·6411 (2)	0·7381 (4)	3·91 (14)
C(10B)	−0·1828 (3)	0·6840 (2)	0·6843 (4)	4·93 (16)
C(11B)	−0·1060 (3)	0·7254 (2)	0·6716 (4)	4·02 (14)
C(12B)	0·1722 (3)	0·8491 (2)	0·7661 (3)	2·76 (11)

Table 2 *(cont.)*

	x	y	z	B_{eq} (Å²)
C(13B)	0·2249 (3)	0·8168 (2)	0·7896 (3)	3·20 (12)
C(14B)	0·3140 (3)	0·8421 (2)	0·8125 (4)	4·22 (14)
C(15B)	0·3485 (3)	0·8988 (2)	0·8105 (4)	5·20 (16)
C(16B)	0·2980 (3)	0·9311 (2)	0·7855 (5)	6·16 (19)
C(17B)	0·2091 (3)	0·9062 (2)	0·7639 (4)	4·93 (16)
C(18B)	0·0272 (3)	0·8258 (2)	0·8452 (3)	2·64 (11)
C(19B)	0·0495 (3)	0·8027 (2)	0·9282 (3)	3·61 (13)
C(20B)	0·0034 (3)	0·8022 (2)	1·0156 (4)	4·33 (14)
C(21B)	−0·0631 (3)	0·8265 (2)	1·0211 (4)	4·30 (14)
C(22B)	−0·0838 (3)	0·8508 (2)	0·9406 (4)	4·27 (14)
C(23B)	−0·0399 (3)	0·8503 (2)	0·8518 (3)	3·49 (13)

weights based on counting-statistics errors do not accurately represent the early-cycle errors in $F_o - F_c$. For later cycles the same weighting scheme was used that was used in the serial full-matrix refinement. Due to strong correlations between the refined variables, it was necessary to damp the shifts calculated in any particular cycle. For this molecule all shifts were damped by 0·5; this value was favored by refinement tests on smaller molecules.

For the first few cycles of refinement emphasis was placed on satisfying the distance restraints (by setting low values for the 'ideal' standard-deviation parameters). As the refinement progressed, the influence of the 'model' on the structure was reduced by raising the 'ideal' standard deviations for both the distance thermal-parameter restraints and finally by completely removing the contributions of the distance restraints from the vector elements. In this manner the final cycles of refinement were influenced primarily by the structure factors. Throughout the refinement all phenyl and *p*-chlorophenyl groups were restrained to be planar to within 0·5 Å. One cycle of serial full-matrix refinement on 72 atoms, 335 variables and 4003 data took 276 CPU seconds while one cycle of restrained refinement on 114 atoms, 343 variables and 6053 data took 22 seconds.

The progress of the minimization of the structure factor residuals in both refinements is shown in Fig. 1. The final R factors for the restrained refinement (carried out using all 6053 reflections) were $R = 10·5$ and $R_w = 6·5\%$. R factors for the same data set as that used in the serial full-matrix refinement (4003 reflections with $|F_o| \le 5·0$) were $R = 6·7$ and $R_w = 5·9\%$ compared to values of 7·1 and 7·2% respectively for the serial full-matrix refinement. The results of the two refinements are shown graphically in Fig. 2. An analysis of the coordinates for the 18 central ring atoms shows excellent agreement between the two refinement procedures. The average deviation for the x, y and z parameters was $0·4\sigma$ and the average deviation for the thermal parameters $0·7\sigma$. For the remaining 54 atoms these values were $1·8\sigma$ and $1·3\sigma$ respectively. However, it should be pointed out that H atoms were included in the restrained refinement and there was a
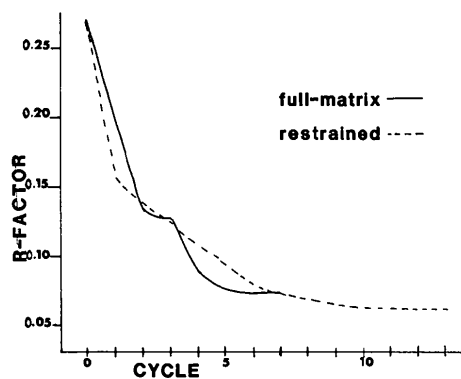
Fig. 1. Comparison of R-factor convergence between the full-matrix and restrained refinements. Full matrix was changed to anisotropic after three cycles.

Table 3. *Hydrogen coordinates with e.s.d.'s in parentheses*

	x	y	z
H(7)	0·145 (2)	0·769 (2)	0·306 (3)
H(8)	0·220 (3)	0·773 (2)	0·163 (3)
H(10)	0·037 (3)	0·632 (2)	0·030 (3)
H(11)	−0·035 (3)	0·631 (2)	0·175 (3)
H(13)	−0·060 (3)	0·570 (2)	0·530 (4)
H(14)	−0·194 (3)	0·516 (2)	0·553 (4)
H(15)	−0·317 (3)	0·524 (2)	0·452 (4)
H(16)	−0·287 (3)	0·588 (2)	0·334 (4)
H(17)	−0·153 (3)	0·639 (2)	0·316 (4)
H(19)	0·172 (3)	0·662 (2)	0·444 (3)
H(20)	0·259 (3)	0·619 (2)	0·387 (4)
H(21)	0·210 (3)	0·535 (2)	0·269 (4)
H(22)	0·051 (3)	0·503 (2)	0·221 (4)
H(23)	−0·032 (3)	0·550 (2)	0·284 (3)
H(7A)	0·171 (3)	0·859 (2)	0·450 (3)
H(8A)	0·310 (3)	0·920 (2)	0·471 (4)
H(10A)	0·218 (3)	1·053 (2)	0·498 (4)
H(11A)	0·077 (3)	0·992 (2)	0·477 (3)
H(13A)	−0·170 (3)	0·825 (2)	0·240 (3)
H(14A)	−0·308 (3)	0·793 (2)	0·261 (3)
H(15A)	−0·362 (3)	0·796 (2)	0·430 (4)
H(16A)	−0·298 (3)	0·836 (2)	0·570 (4)
H(17A)	−0·115 (3)	0·866 (2)	0·539 (3)
H(19A)	−0·088 (3)	0·954 (2)	0·339 (3)
H(20A)	−0·052 (3)	1·019 (2)	0·239 (3)
H(21A)	0·057 (3)	1·018 (2)	0·115 (3)
H(22A)	0·121 (3)	0·946 (2)	0·111 (4)
H(23A)	0·082 (3)	0·879 (2)	0·220 (3)
H(7B)	0·026 (3)	0·680 (2)	0·797 (3)
H(8B)	−0·097 (3)	0·610 (2)	0·817 (3)
H(10B)	−0·232 (3)	0·688 (2)	0·653 (4)
H(11B)	−0·106 (3)	0·755 (2)	0·636 (3)
H(13B)	0·202 (2)	0·778 (2)	0·792 (3)
H(14B)	0·342 (3)	0·816 (2)	0·827 (3)
H(15B)	0·409 (3)	0·914 (2)	0·825 (4)
H(16B)	0·316 (3)	0·970 (2)	0·781 (5)
H(17B)	0·176 (3)	0·930 (2)	0·747 (3)
H(19B)	0·094 (3)	0·786 (2)	0·924 (3)
H(20B)	0·022 (3)	0·785 (2)	1·067 (3)
H(21B)	−0·094 (3)	0·827 (2)	1·080 (3)
H(22B)	−0·128 (3)	0·868 (2)	0·940 (3)
H(23B)	−0·056 (3)	0·867 (2)	0·798 (3)

systematic 'shrinking' of all the phenyl-ring bond lengths from what they were in the serial full-matrix
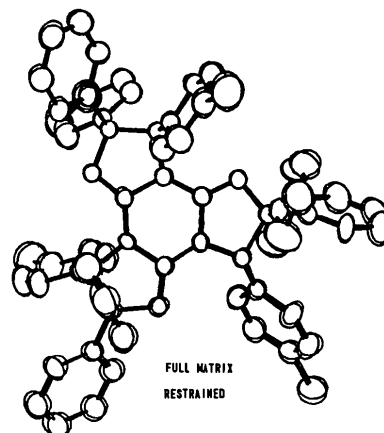

Fig. 2. Conformation of the trimer. Comparison of results from the two methods of refinement. Both were drawn with final refined parameters using *ORTEP* (Johnson, 1965).

refinement. Coordinates and B_{eq} values for the heavy atoms are listed in Table 2. Refined H parameters are listed in Table 3. All data in these tables are from the restrained refinement. Anisotropic thermal parameters, structure factor listings and data detailing the full-matrix refinement are available.[*]

Discussion

Bond lengths and angles for the central heterocyclic ring system and contiguous phenyl-ring atoms are displayed in Fig. 3. For this portion of the molecule there was excellent agreement between the two refinements. The average deviation in bond lengths was 0·004 Å with a maximum of 0·012 Å for the C(3)—C(18) bond. For the angles the average deviation was 0·3° with a maximum of 1·6° for the N(1)—C(5A)—N(4A) angle. In the restrained refinement H atoms were refined anisotropically along with the heavy atoms. The average C—H bond length was 0·93 (7) Å. The average phenyl (C—C) bond length in the serial full-matrix refinement was 1·401 (8) Å and for the restrained refinement it was 1·377 (7) Å. These results are not surprising since it has been noticed quite often that adjacent bond lengths tend to shrink somewhat when H atoms are added. The average C—C—C angle was 119·7 (5)° from the serial full-matrix results and 120·0 (4)° from the restrained results indicating that adding the H atoms caused the area of the phenyl rings to shrink, but did not alter the overall ring geometry. The C—Cl bond lengths were 1·758 (5), 1·706 (5), and 1·741 (5) Å for the serial full-matrix refinement and 1·754 (4), 1·755 (4), 1·751 (4) Å for the restrained refinement. It appears from these results that for most molecules and conditions the restrained refinement can
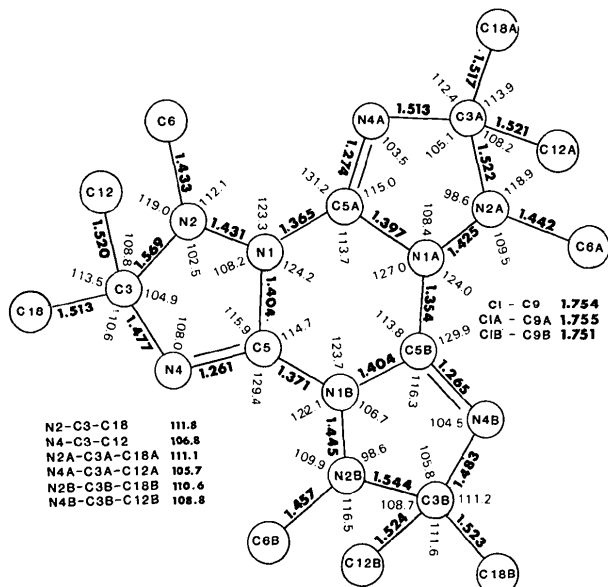
Fig. 3. Bond lengths (Å) and angles (°) for the central heterocyclic ring system of the molecule. Standard deviations are on the order of 0·004 Å for bond lengths and 0·3° for bond angles.
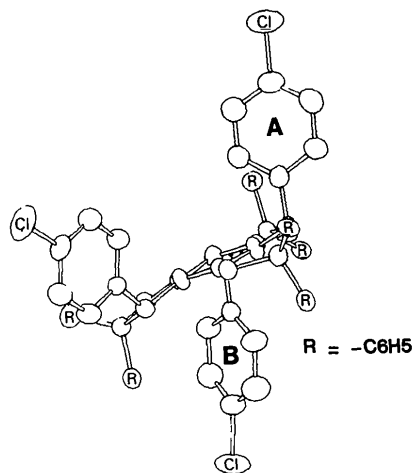

Fig. 4. Conformation of the trimer drawn to illustrate the distribution of the *p*-chlorophenyl rings about the central ring system.

more economically provide parameters and residuals which differ insignificantly for those obtained with serial full-matrix refinement. In addition, for molecules with 50 or more atoms it does allow simultaneous anisotropic refinement of all parameters with small or large sets of data.

Even though the formula of the trimer may be drawn with threefold symmetry the molecule itself is asymmetric with two of the $-C_6H_4Cl$ groups on one side of the central ring system and the third $-C_6H_4Cl$ group on the opposite side. However, each 24-atom segment is approximately related to each of the other two similar moieties. The '*A*' atoms (see Fig. 4) are related to the '*B*' atoms by a rotation of ~65° followed by an inversion. The first 24 atoms are related to the '*B*'

atoms by a rotation of ~73° followed by an inversion. The first 24 atoms are related to the '*A*' atoms by rotation only (~136°). These relationships were determined by calculating the transformations which optimized the superposition of each pair of similar structures, using the program described by Hendrickson (1979). All 24 atoms of each segment were used in the superposition procedure. It is only the central triazine ring which shows approximately threefold symmetry. The three C atoms are displaced slightly below the best plane through the ring (at distances of −0·08, −0·01, and −0·03 Å) and the three N atoms are displaced slightly above the plane (at distances of 0·00, 0·06, and 0·07 Å). As far as intramolecular bond lengths are concerned the only ones of particular interest are the short C=N bonds [1·261 (5), 1·274 (5) and 1·265 (5) Å] radiating from the center ring. 'Normal' C=N bonds are usually in the range 1·29–1·31 Å (Layton, Kross & Fassel, 1956). Packing is influenced only by van der Waals forces with only two intermolecular approaches less than 3·67 Å [C(23*A*)···C(21*B*) at 3·33 Å and C(23*A*)··· C(20*B*) at 3·47 Å]. The only intermolecular approaches less than 4·0 Å between Cl atoms and the rest of the molecule are Cl···C(13*B*) at 3·82 Å and Cl···C(19*B*) at 3·94 Å.

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