

The Crystal and Molecular Structure of Heteroaromatics with *t*-Butyl Groups at *o*-Positions. I. 2,3-Di-*t*-butylquinoxaline at -160°C

BY G. J. VISSER* AND AAFJE VOS

Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Bloemsingel 10, Groningen, The Netherlands

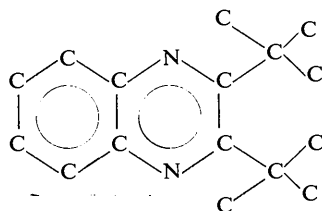
(Received 7 December 1970)

The crystal structure of 2,3-di-*t*-butylquinoxaline ($\text{C}_{16}\text{H}_{22}\text{N}_2$) has been refined with intensities measured at -160°C . The crystals have monoclinic symmetry, space group $P2_1/c$. Unit-cell dimensions are: $a=9.868$ (3), $b=9.883$ (3), $c=28.567$ (6) Å, $\beta=92.62$ (2) $^{\circ}$, $Z=8$. Intensities hkl were collected with an automatic Nonius diffractometer. Anisotropic least-squares refinement with the 8324 non-zero intensities gave $R=0.062$. Carbon and nitrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms were refined with isotropic temperature factors. Estimated standard deviations in the bond lengths and angles not involving the hydrogen atoms are 0.0035 Å and 0.23 $^{\circ}$, respectively. Deviations from planarity observed for the quinoxaline groups of the two molecules are presumably due to inter- rather than intra-molecular forces. No essential differences have been observed between chemically equivalent bonds or angles in the two independent molecules. The $\begin{matrix} > \text{C}(\text{ar})-\text{C}(\text{ar}) < \\ \text{C}(\text{CH}_3)_3 & & \text{C}(\text{CH}_3)_3 \end{matrix}$ part of the molecules

shows some interesting features due to the steric hindrance between the *t*-butyl groups. For the bond $\text{C}(\text{ar})-\text{C}(\text{ar})=1.475$ Å an elongation of 0.06 Å is estimated, whereas the bonds $\text{C}(\text{ar})-\text{C}(\text{CH}_3)_3=1.554$ Å are stretched by about 0.05 Å. The exocyclic angle $\text{C}(\text{ar})-\text{C}(\text{ar})-\text{C}$, 129.7 $^{\circ}$, is 9.7 $^{\circ}$ larger than the usual value of 120 $^{\circ}$. A discussion of the structure of 4,5-di-*t*-butylimidazole at -160°C is given in the paper that follows (part II).

Introduction

The chemical and physical properties of *o*-di-*t*-butyl aromatics, and the synthesis (de Groot, 1967), have aroused considerable interest because of the repulsion energy between the neighbouring *t*-butyl groups. From heats of reaction Arnett, Sanda, Bollinger & Barber (1967) calculated a strain energy of 22.3 kcal.mol $^{-1}$ for the compound 1,2,4-tri-*t*-butylbenzene. To answer the question as to what extent the conformation of the aromatic nucleus is changed by the presence of the *t*-butyl groups, and to estimate the repulsion energy between the groups, the structures of some representative compounds have been determined accurately by means of X-ray diffraction. In the present paper the refinement of the structure of 2,3-di-*t*-butylquinoxaline (DTBQ; $\text{C}_{16}\text{H}_{22}\text{N}_2$) at -160°C is described.



Visser, Vos, de Groot & Wynberg (1968) determined the structure of this compound at room temperature. The paper that follows (part II) deals with the structure determination of 4,5-di-*t*-butylimidazole (DTBI;

$\text{C}_{11}\text{H}_{20}\text{N}_2$) at -160°C . While our work was in progress, the structure of 1,2,4,5-tetra-*t*-butylbenzene (TTBB; $\text{C}_{22}\text{H}_{38}$) was solved by X-ray diffraction at room temperature by van Bruijnsvoort, Eilermann, van der Meer & Stam (1968).

Experimental

The compound 2,3-di-*t*-butylquinoxaline (m.p. 53–54 $^{\circ}$) was prepared in the Laboratory of Organic Chemistry, University of Groningen (de Groot & Wynberg, 1966). Suitable crystals were obtained from a solution in petroleum ether (b.p. 60–80 $^{\circ}$) by evaporating the solvent at room temperature. The crystallographic data at -160°C are listed in Table 1. The angle β was determined on an automated Nonius three-circle diffractometer [$\lambda(\text{Mo } K\alpha)=0.7107$ Å]. The cell dimensions a , b and c were calculated by a least-squares program from the 2θ values obtained from zero-layer line Weissenberg photographs calibrated with NaCl reflexion spots [$\lambda(\text{Cu } K\alpha_1)=1.5418$, $\lambda(\text{Cu } K\alpha_2)=1.54051$ and $\lambda(\text{Cu } K\alpha_3)=1.54433$ Å].

Table 1. Crystallographic data for 2,3-di-*t*-butylquinoxaline (DBTQ) at -160°C

The estimated standard deviations $\times 10^3$ are given in parentheses.

$$a=9.868 \text{ (3)}, \quad b=9.883 \text{ (3)}, \quad c=28.567 \text{ (6) \AA.}$$

$$\alpha=90, \quad \beta=92.62 \text{ (2)}, \quad \gamma=90^{\circ}.$$

Systematic absences: $h0l$ with $l=2n+1$,
 $0k0$ with $k=2n+1$.

Space group $P2_1/c$, $Z=8$, two independent molecules
 $0.88 < d(\text{obs}; 20^{\circ}\text{C}) < 1.298 \text{ g.cm}^{-3}$,
 $d(\text{calc}; -160^{\circ}\text{C})=1.114 \text{ g.cm}^{-3}$
 $\mu(\text{Mo})=0.72 \text{ cm}^{-1}$

* Present address: Rekencentrum, Technische Hogeschool Eindhoven, Postbus 513, Eindhoven, The Netherlands.

The *hkl* intensities were measured at -160°C with Zr-filtered Mo radiation on the automated Nonius diffractometer, the θ - 2θ scan being used. Deviations from linearity of the (scintillation) counting equipment were kept below 1% by use of attenuation filters. The crystal was cooled in a stream of cold nitrogen gas (for equipment used, see van Bolhuis, 1971). All 14677 independent reflexions with $\sin \theta/\lambda \leq 0.86 \text{ \AA}^{-1}$ were measured; 8324 non-zero intensities were obtained. Corrections for Lorentz and polarization effects were made. No absorption corrections were applied, $\mu(\text{Mo } K\alpha)$ being only 0.72 cm^{-1} and the crystal size about $0.5 \times 0.5 \times 0.5 \text{ mm}^3$.

Refinement of the structure

The positions of the carbon and nitrogen atoms obtained at room temperature were used as a starting point for the least-squares refinement. The refinement was done on a TR4 computer with a program working

in block-diagonal approximation (Cruickshank, 1961). After some refinement cycles with the low-order reflexions ($\sin \theta/\lambda \leq 0.4 \text{ \AA}^{-1}$), the positions of the hydrogen atoms were determined from an $[F_o - F_c(\text{C, N})]$ synthesis. In the final cycles, anisotropic temperature factors were used for the heavy atoms and isotropic temperature factors were used for the hydrogen atoms. The scattering factors of C and N were taken from the Cu sphere data of Moore (1963) for $\sin \theta/\lambda \leq 0.7 \text{ \AA}^{-1}$ and from Cromer & Waber (1965) for $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$. For hydrogen Stewart, Davidson & Simpson's (1965) values were used. Different weighting schemes were applied. The parameters obtained with $w=1$ were considered as final parameters since in this case $(\Delta F)^2$ hardly varied with $|F|$. The root-mean-square variation $(\Delta^2)^{1/2}$ in the bond lengths due to changes in the weighting scheme appeared to be 0.0037 \AA . The index *R* decreased to 0.062 for the 8324 reflexions used in the final cycles of the refinement. At the end of the refinement, a difference map of the 8324 reflexions

Table 2. Final coordinates of the two independent DTBQ molecules with standard deviations $\times 10^5$ in parentheses

The numbering of the heavy atoms is given in Fig. 1. The first index assigned to a hydrogen atom indicates the heavy atom to which it is linked; the second index distinguishes between the H atoms linked to the same carbon atom.

Molecule A				Molecule B			
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.21130 (14)	0.22166 (15)	0.24633 (5)	C(17)	0.62771 (14)	0.29434 (14)	-0.01827 (5)
C(2)	0.31554 (14)	0.00992 (15)	0.24208 (5)	C(18)	0.44878 (14)	0.16688 (14)	0.00850 (5)
C(3)	0.37214 (17)	-0.09271 (17)	0.21441 (6)	C(19)	0.32008 (15)	0.10544 (16)	-0.00025 (6)
C(4)	0.42105 (17)	-0.20866 (17)	0.23544 (6)	C(20)	0.25313 (15)	0.05348 (16)	0.03670 (6)
C(5)	0.41453 (16)	-0.22597 (16)	0.28438 (6)	C(21)	0.31071 (16)	0.05921 (17)	0.08293 (6)
C(6)	0.36157 (16)	-0.12766 (16)	0.31200 (6)	C(22)	0.43731 (16)	0.11361 (17)	0.09179 (6)
C(7)	0.31113 (14)	-0.00651 (15)	0.29077 (5)	C(23)	0.50958 (14)	0.16608 (15)	0.05401 (5)
C(8)	0.20812 (14)	0.20812 (14)	0.29776 (5)	C(24)	0.70395 (14)	0.26528 (14)	0.02601 (5)
C(9)	0.15316 (16)	0.33758 (16)	0.21498 (5)	C(25)	0.66116 (15)	0.39372 (16)	-0.05819 (5)
C(10)	0.20140 (22)	0.47963 (18)	0.23017 (7)	C(26)	0.73397 (17)	0.52202 (16)	-0.04011 (6)
C(11)	-0.00262 (18)	0.32475 (21)	0.21057 (7)	C(27)	0.73821 (19)	0.32040 (19)	-0.09629 (6)
C(12)	0.20191 (18)	0.32073 (18)	0.16469 (6)	C(28)	0.52622 (18)	0.44434 (20)	-0.08208 (7)
C(13)	0.16443 (15)	0.30738 (15)	0.33576 (5)	C(29)	0.85707 (14)	0.28467 (15)	0.03983 (5)
C(14)	0.03018 (18)	0.38327 (20)	0.32540 (6)	C(30)	0.95271 (15)	0.27516 (16)	-0.00109 (6)
C(15)	0.28434 (18)	0.40567 (18)	0.34559 (6)	C(31)	0.87697 (16)	0.41856 (17)	0.06670 (6)
C(16)	0.14360 (17)	0.23171 (18)	0.38188 (6)	C(32)	0.90201 (16)	0.17040 (18)	0.07396 (6)
N(1)	0.26430 (13)	0.12433 (13)	0.22143 (4)	N(3)	0.50836 (12)	0.23573 (13)	-0.02618 (4)
N(2)	0.25756 (13)	0.09298 (13)	0.31720 (4)	N(4)	0.63901 (12)	0.21120 (13)	0.06085 (4)
H(3)	0.3748 (23)	-0.0838 (25)	0.1815 (8)	H(19)	0.2872 (22)	0.0977 (23)	-0.0337 (8)
H(4)	0.4582 (22)	-0.2750 (23)	0.2177 (8)	H(20)	0.1672 (22)	0.0105 (23)	0.0339 (8)
H(5)	0.4465 (21)	-0.3105 (23)	0.2970 (8)	H(21)	0.2590 (20)	0.0260 (22)	0.1079 (7)
H(6)	0.3562 (23)	-0.1385 (24)	0.3456 (8)	H(22)	0.4766 (22)	0.1229 (24)	0.1247 (8)
H(10-1)	0.1729 (25)	0.5092 (27)	0.2594 (9)	H(26-1)	0.8253 (21)	0.5072 (23)	-0.0268 (8)
H(10-2)	0.1615 (25)	0.5446 (27)	0.2061 (9)	H(26-2)	0.7365 (22)	0.5903 (23)	-0.0655 (8)
H(10-3)	0.3003 (24)	0.4837 (26)	0.2298 (9)	H(26-3)	0.6863 (21)	0.5595 (22)	-0.0142 (8)
H(11-1)	-0.0469 (21)	0.3273 (23)	0.2385 (8)	H(27-1)	0.8250 (22)	0.2824 (23)	-0.0842 (8)
H(11-2)	-0.0354 (24)	0.3990 (26)	0.1910 (9)	H(27-2)	0.6849 (22)	0.2435 (24)	-0.1078 (8)
H(11-3)	-0.0274 (23)	0.2359 (24)	0.1952 (8)	H(27-3)	0.7503 (24)	0.3832 (26)	-0.1218 (9)
H(12-1)	0.3003 (24)	0.3283 (24)	0.1624 (8)	H(28-1)	0.4739 (24)	0.3715 (26)	-0.0955 (9)
H(12-2)	0.1634 (22)	0.1468 (24)	0.1468 (8)	H(28-2)	0.5447 (23)	0.5133 (25)	-0.1060 (8)
H(12-3)	0.1731 (21)	0.2353 (23)	0.1512 (8)	H(28-3)	0.4702 (25)	0.4841 (28)	-0.0586 (9)
H(14-1)	0.0091 (22)	0.4393 (24)	0.3521 (8)	H(30-1)	0.9376 (21)	0.1884 (22)	-0.0179 (7)
H(14-2)	-0.0443 (21)	0.3204 (23)	0.3197 (8)	H(30-2)	0.9439 (20)	0.3486 (22)	-0.0233 (7)
H(14-3)	0.0306 (22)	0.4475 (24)	0.2993 (8)	H(30-3)	1.0479 (21)	0.2707 (23)	0.0114 (8)
H(15-1)	0.3079 (21)	0.4523 (22)	0.3191 (8)	H(31-1)	0.8203 (22)	0.4205 (23)	0.0944 (8)
H(15-2)	0.2602 (23)	0.4718 (24)	0.3684 (8)	H(31-2)	0.9729 (23)	0.4257 (25)	0.0800 (8)
H(15-3)	0.3665 (23)	0.3533 (25)	0.3577 (8)	H(31-3)	0.8524 (19)	0.4970 (21)	0.0493 (7)
H(16-1)	0.2249 (22)	0.1833 (24)	0.3931 (8)	H(32-1)	0.8562 (21)	0.1674 (23)	0.1023 (8)
H(16-2)	0.1121 (22)	0.2957 (24)	0.4044 (8)	H(32-2)	0.8846 (19)	0.0756 (21)	0.0605 (7)
H(16-3)	0.0768 (22)	0.1580 (24)	0.3773 (8)	H(32-3)	1.0017 (21)	0.1808 (23)	0.0821 (8)

revealed maxima ranging from 0.25 to 0.55 (standard deviation 0.14) e.Å⁻³ on the bonds between the heavy atoms. The final parameters are listed in Tables 2 and 3, with standard deviations as calculated by the least-squares program. Table 4 gives a list of $|F_o|^2$ and $|F_c|^2$.

An analysis of the low-temperature anisotropic thermal parameters of the heavy atoms according to Pawley (1963) showed that the two independent DTBQ molecules cannot be considered as rigid bodies. The rigid-body approximation appeared to be valid, however, for the quinoxaline system of the molecules. When considering only the quinoxaline part in the analysis, the differences between $U(\text{obs})$ and $U(\text{calc})$ appeared to vary from zero to twice the e.s.d. in $U(\text{obs})$. The deviations from the rigid-body behaviour of the complete DTBQ molecules could not be interpreted in terms of librations of the t-butyl groups around the C(ring)–C(t-butyl) bonds. The bond lengths and angles given in Table 5 are not corrected for

libration effects. Estimated values for the corrections in the bond lengths for the quinoxaline group vary from 0.001 to 0.004 Å.

Discussion of the structure

Arrangement of the molecules

The projection of the molecules onto the (010) plane, and the numbering of the atoms, are given in Fig. 1. The two independent molecules are labeled *A* and *B*, the t-butyl groups of *A* are indicated by *P* and *Q* and those of *B* by *R* and *S*. In Fig. 2 we have projected along the *z* axis the symmetrically related molecules *B* and *B'* and, in part, some molecules of type *A*, viz. *A''*, related to *A* by the twofold screw-axis [$\frac{1}{2}, y, \frac{1}{2}$] and *A'''* related to *A''* by an inversion centre. Short intermolecular distances are indicated by dashed lines in Figs. 1 & 2. In general, we considered as short distances those smaller than 0.2 Å plus the sum of the relevant van der Waals radii (1.7, 1.5 and 1.2 Å for C, N and H

Table 3. *Thermal parameters*

The anisotropic temperature factor of the heavy atoms is defined as $\exp[-2\pi^2(h^2a^*U_{11} + k^2b^*U_{22} + l^2c^*U_{33} + 2ha^*kb^*U_{12} + 2kb^*lc^*U_{23} + 2ha^*lc^*U_{13})]$. For the hydrogen atoms the isotropic temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$ is used. The $B(H)$ values vary from 1.3 to 3.7 Å².

Molecule <i>A</i>	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0.0142 (5)	0.0149 (6)	0.0144 (6)	-0.0019 (9)	0.0017 (9)	0.0012 (9)
C(2)	0.0156 (5)	0.0148 (6)	0.0157 (6)	0.0009 (9)	-0.0005 (10)	0.0014 (9)
C(3)	0.0274 (8)	0.0198 (7)	0.0180 (7)	0.0107 (12)	-0.0029 (11)	0.0065 (11)
C(4)	0.0259 (7)	0.0169 (7)	0.0242 (7)	0.0110 (11)	-0.0049 (11)	0.0055 (12)
C(5)	0.0216 (7)	0.0163 (6)	0.0266 (7)	0.0088 (11)	0.0013 (11)	-0.0014 (11)
C(6)	0.0219 (7)	0.0170 (6)	0.0185 (6)	0.0088 (10)	0.0022 (10)	0.0010 (10)
C(7)	0.0149 (5)	0.0148 (6)	0.0146 (6)	-0.0006 (9)	0.0006 (9)	-0.0009 (9)
C(8)	0.0136 (5)	0.0143 (6)	0.0146 (6)	-0.0006 (9)	0.0012 (9)	0.0022 (8)
C(9)	0.0208 (6)	0.0170 (6)	0.0174 (6)	0.0080 (10)	0.0082 (10)	0.0032 (10)
C(10)	0.0464 (11)	0.0169 (7)	0.0246 (8)	-0.0016 (14)	0.0065 (12)	0.0103 (15)
C(11)	0.0223 (7)	0.0371 (10)	0.0255 (8)	0.0176 (14)	0.0121 (15)	-0.0041 (12)
C(12)	0.0317 (8)	0.0234 (7)	0.0171 (7)	0.0120 (13)	0.0100 (12)	0.0047 (12)
C(13)	0.0184 (6)	0.0163 (6)	0.0162 (6)	0.0041 (10)	-0.0023 (10)	0.0059 (9)
C(14)	0.0255 (8)	0.0298 (9)	0.0236 (8)	0.0222 (13)	-0.0005 (13)	0.0090 (12)
C(15)	0.0287 (8)	0.0218 (7)	0.0262 (8)	-0.0093 (13)	-0.0135 (13)	0.0100 (12)
C(16)	0.0264 (7)	0.0246 (7)	0.0177 (7)	0.0091 (12)	0.0020 (12)	0.0123 (11)
N(1)	0.0190 (5)	0.0167 (5)	0.0148 (5)	0.0038 (9)	0.0025 (9)	0.0008 (8)
N(2)	0.0178 (5)	0.0153 (5)	0.0153 (5)	0.0022 (9)	0.0005 (9)	0.0017 (8)
Molecule <i>B</i>	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(17)	0.0158 (5)	0.0138 (5)	0.0138 (5)	-0.0020 (9)	0.0011 (9)	0.0023 (9)
C(18)	0.0144 (5)	0.0124 (5)	0.0165 (6)	-0.0012 (9)	0.0010 (9)	0.0007 (9)
C(19)	0.0161 (6)	0.0181 (6)	0.0223 (7)	-0.0059 (10)	0.0010 (11)	-0.0048 (10)
C(20)	0.0152 (6)	0.0169 (6)	0.0307 (8)	-0.0055 (10)	0.0029 (12)	0.0029 (11)
C(21)	0.0185 (6)	0.0192 (7)	0.0251 (7)	-0.0053 (11)	0.0034 (11)	0.0132 (11)
C(22)	0.0194 (6)	0.0216 (7)	0.0175 (6)	-0.0076 (11)	0.0034 (11)	0.0060 (10)
C(23)	0.0141 (5)	0.0148 (6)	0.0162 (6)	-0.0030 (9)	-0.0008 (10)	0.0023 (9)
C(24)	0.0144 (5)	0.0141 (5)	0.0136 (5)	-0.0021 (9)	0.0015 (9)	-0.0002 (8)
C(25)	0.0189 (6)	0.0181 (6)	0.0159 (6)	-0.0038 (10)	0.0084 (10)	0.0026 (10)
C(26)	0.0263 (7)	0.0154 (6)	0.0221 (7)	-0.0020 (11)	0.0049 (11)	0.0071 (11)
C(27)	0.0325 (8)	0.0258 (8)	0.0155 (6)	-0.0075 (13)	-0.0018 (12)	0.0070 (11)
C(28)	0.0243 (8)	0.0325 (9)	0.0279 (8)	-0.0054 (14)	0.0316 (14)	-0.0110 (12)
C(29)	0.0144 (5)	0.0164 (6)	0.0157 (6)	-0.0072 (9)	0.0010 (10)	-0.0009 (9)
C(30)	0.0163 (6)	0.0194 (7)	0.0214 (7)	-0.0054 (10)	-0.0010 (11)	0.0032 (10)
C(31)	0.0219 (7)	0.0192 (7)	0.0206 (7)	-0.0097 (11)	-0.0074 (11)	0.0021 (11)
C(32)	0.0182 (6)	0.0248 (7)	0.0243 (7)	-0.0096 (11)	0.0138 (12)	-0.0091 (11)
N(3)	0.0156 (5)	0.0164 (5)	0.0156 (5)	-0.0044 (8)	0.0028 (9)	-0.0006 (8)
N(4)	0.0157 (5)	0.0185 (6)	0.0146 (5)	-0.0059 (9)	0.0006 (9)	0.0009 (8)

Table 4. Observed and calculated [F]D values

Table with multiple columns containing numerical data, likely representing observed and calculated values for various compounds. The table is organized into several sections, possibly corresponding to different chemical groups or conditions.

Table 4 (cont.)

A large table of numerical data with multiple columns and rows, containing various numbers and some text labels like '1. 6.L.', '2. 6.L.', etc.

Table 4 (cont.)

Table with multiple columns of numerical data, organized into sections labeled 4, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100. Each section contains a list of numbers, some with sub-labels like 'a', 'b', 'c', 'd', 'e', 'f', 'g', 'h', 'i', 'j', 'k', 'l', 'm', 'n', 'o', 'p', 'q', 'r', 's', 't', 'u', 'v', 'w', 'x', 'y', 'z' and '10.0 L'.

of *B* (or *B'*) and some neighbouring hydrogen atoms. The quinoxaline group of *A''* (Fig. 1) lies only close to the *t*-butyl group *P* of *A*. As to the surroundings of the *t*-butyl groups, there exist no remarkable differences between molecules *A* and *B*. Most short distances are observed at *Q* and *S* (see *S'* and *Q''* in Fig. 2).

The structure of the molecules

The values of the bond lengths, angles and some short intramolecular distances between the heavy atoms are given in Table 5. The C–H bond lengths range from 0.92 to 1.02 (e.s.d. 0.02 Å). The standard deviations in the bond lengths and angles are estimated at 0.0035 Å and 0.23° respectively; they account for the standard deviations calculated by the least-squares program and for the errors in the positions of the heavy atoms due

to uncertainties in the weighting scheme and in the positions of the hydrogen atoms.

Table 6 shows that the two quinoxaline groups are not completely planar. The deviations from planarity appear to be much smaller for *A*, which lies relatively free in the crystal structure, than for *B*. Therefore we are inclined to ascribe the non-planar structure of the quinoxaline groups to inter- rather than to intramolecular forces. As is seen from Table 5, chemically equivalent bonds or angles of the two quinoxaline systems have essentially the same values, which in further discussions are considered as average values. Rather large differences, up to 3.6°, appear to occur, however, between corresponding angles in the *t*-butyl groups. All C(tb)–CH₃ bond lengths equal their average value of 1.541 Å [C(tb) = quaternary carbon

Table 5. Bond lengths, angles and short intramolecular non-bonded distances

(a) Bond lengths and angles for the quinoxaline group				(b) Bond lengths and angles for the <i>t</i> -butyl groups			
Molecule <i>A</i>		Molecule <i>B</i>		Molecule <i>A</i>		Molecule <i>B</i>	
C(1)–N(1)	1.319 Å	C(17)–N(3)	1.323 Å	C(1)–C(9)	1.548 Å	C(17)–C(25)	1.552 Å
C(8)–N(2)	1.323	C(24)–N(4)	1.321	C(9)–C(10)	1.539	C(25)–C(26)	1.535
N(1)–C(2)	1.362	N(3)–C(18)	1.358	C(9)–C(11)	1.542	C(25)–C(27)	1.537
N(2)–C(7)	1.361	N(4)–C(23)	1.359	C(9)–C(12)	1.545	C(25)–C(28)	1.551
C(2)–C(3)	1.416	C(18)–C(19)	1.420	C(8)–C(13)	1.558	C(24)–C(29)	1.556
C(7)–C(6)	1.422	C(23)–C(22)	1.419	C(13)–C(14)	1.539	C(29)–C(30)	1.539
C(3)–C(4)	1.371	C(19)–C(20)	1.370	C(13)–C(15)	1.547	C(29)–C(31)	1.538
C(6)–C(5)	1.370	C(22)–C(21)	1.373	C(13)–C(16)	1.537	C(29)–C(32)	1.544
C(1)–C(8)	1.480	C(17)–C(24)	1.470				
C(2)–C(7)	1.403	C(18)–C(23)	1.407	C(1)–C(9)–C(10)	114.23°	C(17)–C(25)–C(26)	112.80°
C(4)–C(5)	1.413	C(20)–C(21)	1.415	C(1)–C(9)–C(11)	109.16	C(17)–C(25)–C(27)	110.53
				C(1)–C(9)–C(12)	109.59	C(17)–C(25)–C(28)	108.68
N(1)–C(1)–C(8)	118.83°	N(3)–C(17)–C(24)	118.56°	C(10)–C(9)–C(11)	113.11	C(26)–C(25)–C(27)	112.86
N(2)–C(8)–C(1)	118.99	N(4)–C(24)–C(17)	118.72	C(10)–C(9)–C(12)	104.78	C(26)–C(25)–C(28)	105.12
N(1)–C(1)–C(9)	111.93	N(3)–C(17)–C(25)	111.67	C(11)–C(9)–C(12)	105.48	C(27)–C(25)–C(28)	106.44
N(2)–C(8)–C(13)	111.06	N(4)–C(24)–C(29)	110.95	C(8)–C(13)–C(14)	116.43	C(24)–C(29)–C(30)	114.96
C(8)–C(1)–C(9)	129.17	C(24)–C(17)–C(25)	129.66	C(8)–C(13)–C(15)	107.45	C(24)–C(29)–C(31)	109.45
C(1)–C(8)–C(13)	129.75	C(17)–C(24)–C(29)	130.32	C(8)–C(13)–C(16)	109.51	C(24)–C(29)–C(32)	108.53
C(1)–N(1)–C(2)	121.37	C(17)–N(3)–C(18)	120.45	C(14)–C(13)–C(15)	111.93	C(30)–C(29)–C(31)	111.29
C(8)–N(2)–C(7)	121.17	C(24)–N(4)–C(23)	120.64	C(14)–C(13)–C(16)	104.73	C(30)–C(29)–C(32)	105.47
N(1)–C(2)–C(3)	120.06	N(3)–C(18)–C(19)	119.98	C(15)–C(13)–C(16)	106.33	C(31)–C(29)–C(32)	106.73
N(2)–C(7)–C(6)	120.59	N(4)–C(23)–C(22)	120.83				
N(1)–C(2)–C(7)	119.85	N(3)–C(18)–C(23)	119.77	(c) Non-bonded intramolecular distances smaller than 3.50 Å between the carbon atoms of different <i>t</i> -butyl groups			
N(2)–C(7)–C(2)	119.78	N(4)–C(23)–C(18)	119.31	C(9)–C(13)	3.460 Å	C(25)–C(29)	3.499 Å
C(3)–C(2)–C(7)	120.09	C(19)–C(18)–C(23)	120.04	C(9)–C(14)	3.461	C(25)–C(30)	3.447
C(6)–C(7)–C(2)	119.62	C(22)–C(23)–C(18)	119.81	C(10)–C(13)	3.497	C(26)–C(29)	3.455
C(2)–C(3)–C(4)	119.59	C(18)–C(19)–C(20)	118.92	C(10)–C(14)	3.403	C(26)–C(30)	3.411
C(7)–C(6)–C(5)	119.13	C(23)–C(22)–C(21)	119.19	C(10)–C(15)	3.439	C(26)–C(31)	3.457
C(3)–C(4)–C(5)	120.24	C(19)–C(20)–C(21)	121.12	C(11)–C(14)	3.332	C(27)–C(30)	3.399
C(6)–C(5)–C(4)	121.32	C(22)–C(21)–C(20)	120.73				

Table 6. Atomic distances to the best planes through the quinoxaline groups

The equations of the planes are referred to the axes $X = x \sin \beta$, $Y = y$ and $Z = z + x \cos \beta$ (in Å) and are given by:

$$0.9012X + 0.4263Y + 0.0785Z = 3.370 \text{ (molecule } A) \text{ and} \\ -0.4053X + 0.8833Y + 0.2358Z = -0.280 \text{ (molecule } B).$$

Molecule <i>A</i>		Molecule <i>B</i>	
C(1)	–0.014 Å	C(8)	0.004 Å
N(1)	–0.011	C(9)	–0.110
C(2)	0.007	C(10)	0.949
C(3)	0.013	C(11)	–1.553
C(4)	0.005	C(12)	0.137
C(5)	–0.016	C(13)	0.133
C(6)	–0.009	C(14)	–0.758
C(7)	0.008	C(15)	1.630
N(2)	0.012	C(16)	–0.267
		C(17)	0.152 Å
		N(3)	0.076
		C(18)	–0.047
		C(19)	–0.114
		C(20)	–0.044
		C(21)	0.081
		C(22)	0.096
		C(23)	0.003
		N(4)	–0.088
		C(24)	–0.116 Å
		C(25)	0.613
		C(26)	1.556
		C(27)	–0.599
		C(28)	1.448
		C(29)	–0.482
		C(30)	–1.233
		C(31)	0.786
		C(32)	–1.434

atom of t-butyl group]. Finally, we note that the structures of the DTBQ molecules at low and room temperatures (Visser *et al.*, 1968) do not show significant differences.

Comparison of the bond lengths in DTBQ with those in analogous aromatic compounds bearing small substituents (anthracene: Mason, 1964; naphthalene: Cruickshank, 1957; acridine: Phillips, Ahmed & Barnes, 1960; α -phenazine: Hirshfeld & Schmidt, 1957) shows that most of the bonds in the quinoxaline system do not deviate from the expected values, but that the bonds of type C(1)–C(8) are exceptionally long. For small substituents, equal values are expected for the bonds C(1)–C(8) and C(4)–C(5), whereas in DTBQ the bonds of type C(1)–C(8), which average 1.475 Å, are 0.06 Å longer than the bonds of type C(4)–C(5), which average 1.414 Å. We ascribe this elongation to the presence of the large t-butyl groups. Also the bonds of type C(1)–C(tb), which average 1.554 Å, appear to be stretched. A stretching of 0.05 Å was estimated by comparing the C–C(tb) bond lengths with the weighted average value of 1.505 Å observed for a number of C(ar)–CH₃ bonds (Visser, 1969) and with the length of 1.505 (standard deviation 0.003 Å) found in isobutylene (Bartell & Bonham, 1960). In TTBB the bond corresponding to C(1)–C(8) is 0.02 Å longer than the C–C bonds in benzene (Bacon, Curry & Wilson, 1964), whereas the stretching of C–C(tb) is estimated at 0.06 Å.

In addition to the elongation of some bonds, a bending of some of the valence angles is observed. The angles of type C(1)–C(8)–C(tb), average value 129.7°, are 9.7° larger than the expected value of 120°. This again influences the geometry of the pyrazine ring, as is noticed from the value of the angle C–N–C (120.9°) which is large compared with the corresponding angle in α -phenazine (116.3°; Hirshfeld & Schmidt, 1957) and in acridine (117.9°; Phillips, Ahmed & Barnes, 1960) and appreciably larger than the average value of 115.7(±0.2°) given by Singh (1965) for angles of this type in 20 structures. In TTBB the C–C–C angles corresponding to C(8)–C(1)–C(tb) and C–N–C are 131.0 and 129.5° respectively.

The distances between the two t-butyl groups and those between each of these groups and the quinoxaline system are discussed in the paper that follows (part II).

We are indebted to Professor H. Wynberg for suggesting the problem and to Professor E. H. Wiebenga for his continuous interest. Thanks are due to Mr F. van Bolhuis for his valuable help during the measurements and to the staff of the Computing Centre of the University of Groningen for operating the TR4 computer.

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